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CERTIFICATION REPORT

Certification of the uranium hexafluoride (UF_6) isotopic composition: The IRMM-019 to IRMM-029 series

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Certain commercial equipment, instruments, and materials are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the European Commission, nor does it imply that the material or equipment is necessarily the best available for the purpose.

Summary

This report describes the re-determination and certification of the IRMM-019 to IRMM-029 series of uranium hexafluoride (UF_6) reference materials certified for the uranium isotopic composition. The values were assigned following ISO Guide 34:2009 [1].

The IRMM-019 to IRMM-029 series was originally produced and certified in the 1980's-1990's. Since, the materials are stored in monel ampoules. Upon customer request, UF_6 gas is distilled from a mother ampoule into a daughter ampoule, the isotopic composition is verified by Gas Source Mass Spectrometry (GSMS) and the daughter ampoule is sent to the customer. For the purpose of this project, the UF_6 materials were converted into uranium nitrate solutions to perform the homogeneity and characterisation studies.

Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006 [2].

The materials were characterised by Thermal Ionisation Mass Spectrometry (TIMS) using newly established measurement procedures such as the Modified Total Evaporation (MTE) and Double Spike (DS) methods, and with a new set of certified uranium isotope reference materials, which were prepared by gravimetrical mixing of highly enriched ^{233}U, ^{235}U, ^{236}U and ^{238}U oxides or solutions. The results of the characterisation measurements were also confirmed by GSMS measurements using the original UF_6 gases.

Uncertainties of the certified values were estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [3] and include uncertainties related to the characterisation measurements and the homogeneity study.

The materials are intended for the calibration of methods, quality control purposes, and the assessment of method performance for isotope mass spectrometry. As with any certified reference material, they can also be used for validation studies. The CRMs are available in monel ampoules. Based on physical reasons, there is no minimum sample intake to be taken into account.

The following values were assigned:

	Isotope amount ratios	
	Certified values [mol/mol]	Uncertainty [3)] [mol/mol]
IRMM-019[1)]		
$n(^{234}\text{U})/n(^{238}\text{U})$	0.00000685	0.00000004
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0016775	0.0000005
$n(^{236}\text{U})/n(^{238}\text{U})$	0.00003652	0.00000009
IRMM-020[1)]		
$n(^{234}\text{U})/n(^{238}\text{U})$	0.00001192	0.00000006
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0020957	0.0000006
$n(^{236}\text{U})/n(^{238}\text{U})$	0.00028615	0.00000011
IRMM-021[2)]		
$n(^{234}\text{U})/n(^{238}\text{U})$	0.00002485	0.00000008
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0044052	0.0000008
$n(^{236}\text{U})/n(^{238}\text{U})$	0.0000000266	0.0000000008

IRMM-022[2]		
$n(^{234}U)/n(^{238}U)$	0.00005328	0.00000009
$n(^{235}U)/n(^{238}U)$	0.0072562	0.0000012
$n(^{236}U)/n(^{238}U)$	0.0000002415	0.0000000026
IRMM-023[2]		
$n(^{234}U)/n(^{238}U)$	0.00033950	0.00000011
$n(^{235}U)/n(^{238}U)$	0.033881	0.000006
$n(^{236}U)/n(^{238}U)$	0.0000001153	0.0000000017
IRMM-024[1]		
$n(^{234}U)/n(^{238}U)$	0.00029075	0.00000014
$n(^{235}U)/n(^{238}U)$	0.053254	0.000016
$n(^{236}U)/n(^{238}U)$	0.00051696	0.00000013
IRMM-025[1]		
$n(^{234}U)/n(^{238}U)$	0.00012245	0.00000009
$n(^{235}U)/n(^{238}U)$	0.020436	0.000006
$n(^{236}U)/n(^{238}U)$	0.00014839	0.00000009
IRMM-026[1]		
$n(^{234}U)/n(^{238}U)$	0.00014941	0.00000010
$n(^{235}U)/n(^{238}U)$	0.025679	0.000008
$n(^{236}U)/n(^{238}U)$	0.00020730	0.00000011
IRMM-027[1]		
$n(^{234}U)/n(^{238}U)$	0.00023159	0.00000013
$n(^{235}U)/n(^{238}U)$	0.041717	0.000013
$n(^{236}U)/n(^{238}U)$	0.00038739	0.00000012
IRMM-028[1]		
$n(^{234}U)/n(^{238}U)$	0.00061041	0.00000027
$n(^{235}U)/n(^{238}U)$	0.037576	0.000012
$n(^{236}U)/n(^{238}U)$	0.0051943	0.0000012
IRMM-029[1]		
$n(^{234}U)/n(^{238}U)$	0.0008444	0.0000004
$n(^{235}U)/n(^{238}U)$	0.044052	0.000014
$n(^{236}U)/n(^{238}U)$	0.0105563	0.0000023

[1] The certified values are traceable to the International System of units (SI) via IRMM-074/10.

[2] The certified values are traceable to the International System of units (SI) via IRMM-3636a.

[3] The uncertainty is the expanded uncertainty with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

	Isotope amount fraction	
	Certified values [1)] [mol/mol]	Uncertainty [2)] [mol/mol]
IRMM-019		
$n(^{234}U)/n(U) \times 100$	0.000683	0.000004
$n(^{235}U)/n(U) \times 100$	0.16746	0.00005
$n(^{236}U)/n(U) \times 100$	0.003646	0.000009
$n(^{238}U)/n(U) \times 100$	99.82821	0.00005
IRMM-020		
$n(^{234}U)/n(U) \times 100$	0.001189	0.000005
$n(^{235}U)/n(U) \times 100$	0.20907	0.00006
$n(^{236}U)/n(U) \times 100$	0.028547	0.000011
$n(^{238}U)/n(U) \times 100$	99.76119	0.00007
IRMM-021		
$n(^{234}U)/n(U) \times 100$	0.002474	0.000008
$n(^{235}U)/n(U) \times 100$	0.43858	0.00008
$n(^{236}U)/n(U) \times 100$	0.00000265	0.00000008
$n(^{238}U)/n(U) \times 100$	99.55895	0.00008
IRMM-022		
$n(^{234}U)/n(U) \times 100$	0.005289	0.000009
$n(^{235}U)/n(U) \times 100$	0.72035	0.00012
$n(^{236}U)/n(U) \times 100$	0.00002397	0.00000025
$n(^{238}U)/n(U) \times 100$	99.27433	0.00012
IRMM-023		
$n(^{234}U)/n(U) \times 100$	0.032827	0.000011
$n(^{235}U)/n(U) \times 100$	3.2760	0.0006
$n(^{236}U)/n(U) \times 100$	0.00001115	0.00000016
$n(^{238}U)/n(U) \times 100$	96.6911	0.0006
IRMM-024		
$n(^{234}U)/n(U) \times 100$	0.027584	0.000013
$n(^{235}U)/n(U) \times 100$	5.0523	0.0014
$n(^{236}U)/n(U) \times 100$	0.049045	0.000013
$n(^{238}U)/n(U) \times 100$	94.8711	0.0014
IRMM-025		
$n(^{234}U)/n(U) \times 100$	0.011997	0.000009
$n(^{235}U)/n(U) \times 100$	2.0021	0.0006
$n(^{236}U)/n(U) \times 100$	0.014538	0.000009
$n(^{238}U)/n(U) \times 100$	97.9714	0.0006
IRMM-026		
$n(^{234}U)/n(U) \times 100$	0.014562	0.000010
$n(^{235}U)/n(U) \times 100$	2.5027	0.0008
$n(^{236}U)/n(U) \times 100$	0.020204	0.000011

$n(^{238}U)/n(U)$ ×100	97.4625	0.0008
IRMM-027		
$n(^{234}U)/n(U)$ ×100	0.022218	0.000013
$n(^{235}U)/n(U)$ ×100	4.0023	0.0012
$n(^{236}U)/n(U)$ ×100	0.037166	0.000011
$n(^{238}U)/n(U)$ ×100	95.9383	0.0012
IRMM-028		
$n(^{234}U)/n(U)$ ×100	0.058503	0.000026
$n(^{235}U)/n(U)$ ×100	3.6014	0.0011
$n(^{236}U)/n(U)$ ×100	0.49783	0.00011
$n(^{238}U)/n(U)$ ×100	95.8423	0.0011
IRMM-029		
$n(^{234}U)/n(U)$ ×100	0.08001	0.00004
$n(^{235}U)/n(U)$ ×100	4.1737	0.0012
$n(^{236}U)/n(U)$ ×100	1.00017	0.00021
$n(^{238}U)/n(U)$ ×100	94.7461	0.0012

1) These values are calculated using the isotope amount ratios and they are therefore traceable to the SI.

2) The uncertainty is the expanded uncertainty with a coverage factor k = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

	Isotope mass fraction	
	Certified values 1)2) [g/g]	Uncertainty 3) [g/g]
IRMM-019		
$m(^{234}U)/m(U)$ ×100	0.000672	0.000004
$m(^{235}U)/m(U)$ ×100	0.16535	0.00005
$m(^{236}U)/m(U)$ ×100	0.003615	0.000009
$m(^{238}U)/m(U)$ ×100	99.83036	0.00005
IRMM-020		
$m(^{234}U)/m(U)$ ×100	0.001169	0.000005
$m(^{235}U)/m(U)$ ×100	0.20644	0.00006
$m(^{236}U)/m(U)$ ×100	0.028307	0.000011
$m(^{238}U)/m(U)$ ×100	99.76409	0.00007
IRMM-021		
$m(^{234}U)/m(U)$ ×100	0.002432	0.000008
$m(^{235}U)/m(U)$ ×100	0.43306	0.00007
$m(^{236}U)/m(U)$ ×100	0.00000262	0.00000008
$m(^{238}U)/m(U)$ ×100	99.56450	0.00007
IRMM-022		
$m(^{234}U)/m(U)$ ×100	0.005200	0.000009
$m(^{235}U)/m(U)$ ×100	0.71132	0.00012
$m(^{236}U)/m(U)$ ×100	0.00002377	0.00000025

$m(^{238}U)/m(U) \times 100$	99.28346	0.00012
IRMM-023		
$m(^{234}U)/m(U) \times 100$	0.032288	0.000011
$m(^{235}U)/m(U) \times 100$	3.2360	0.0005
$m(^{236}U)/m(U) \times 100$	0.00001106	0.00000016
$m(^{238}U)/m(U) \times 100$	96.7317	0.0005
IRMM-024		
$m(^{234}U)/m(U) \times 100$	0.027137	0.000013
$m(^{235}U)/m(U) \times 100$	4.9917	0.0014
$m(^{236}U)/m(U) \times 100$	0.048663	0.000013
$m(^{238}U)/m(U) \times 100$	94.9325	0.0014
IRMM-025		
$m(^{234}U)/m(U) \times 100$	0.011798	0.000009
$m(^{235}U)/m(U) \times 100$	1.9773	0.0006
$m(^{236}U)/m(U) \times 100$	0.014419	0.000009
$m(^{238}U)/m(U) \times 100$	97.9965	0.0006
IRMM-026		
$m(^{234}U)/m(U) \times 100$	0.014321	0.000010
$m(^{235}U)/m(U) \times 100$	2.4719	0.0007
$m(^{236}U)/m(U) \times 100$	0.020040	0.000011
$m(^{238}U)/m(U) \times 100$	97.4937	0.0007
IRMM-027		
$m(^{234}U)/m(U) \times 100$	0.021855	0.000012
$m(^{235}U)/m(U) \times 100$	3.9538	0.0012
$m(^{236}U)/m(U) \times 100$	0.036871	0.000011
$m(^{238}U)/m(U) \times 100$	95.9875	0.0012
IRMM-028		
$m(^{234}U)/m(U) \times 100$	0.057547	0.000026
$m(^{235}U)/m(U) \times 100$	3.5577	0.0011
$m(^{236}U)/m(U) \times 100$	0.49389	0.00011
$m(^{238}U)/m(U) \times 100$	95.8909	0.0011
IRMM-029		
$m(^{234}U)/m(U) \times 100$	0.07871	0.00004
$m(^{235}U)/m(U) \times 100$	4.1236	0.0012
$m(^{236}U)/m(U) \times 100$	0.99237	0.00021
$m(^{238}U)/m(U) \times 100$	94.8054	0.0012

1) These values are calculated using the isotope amount ratios and they are therefore traceable to the SI.

2) These values are calculated using the values listed below from *Audi et al., The AME 2003 atomic mass evaluation, Nuclear Physics A 729, 337-676, 2003:*

$M(^{234}U) = 234.0409521 \pm 0.0000040\ g \cdot mol^{-1}$
$M(^{235}U) = 235.0439299 \pm 0.0000040\ g \cdot mol^{-1}$
$M(^{236}U) = 236.0455680 \pm 0.0000040\ g \cdot mol^{-1}$
$M(^{238}U) = 238.0507882 \pm 0.0000040\ g \cdot mol^{-1}$

[3] The uncertainty is the expanded uncertainty with a coverage factor *k* = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

	Uranium molar mass	
	Certified values [1)2)] [g·mol^{-1}]	Uncertainty [3)] [g·mol^{-1}]
IRMM-019 M(U)	238.045652	0.000005
IRMM-020 M(U)	238.043882	0.000005
IRMM-021 M(U)	238.037502	0.000005
IRMM-022 M(U)	238.028916	0.000006
IRMM-023 M(U)	237.950966	0.000016
IRMM-024 M(U)	237.89678	0.00005
IRMM-025 M(U)	237.989815	0.000017
IRMM-026 M(U)	237.974545	0.000022
IRMM-027 M(U)	237.92881	0.00004
IRMM-028 M(U)	237.93017	0.00004
IRMM-029 M(U)	237.90203	0.00004

[1)] These values are calculated using the isotope amount ratios and they are therefore traceable to SI.

[2)] These values are calculated using the values listed below from *Audi et al., The AME 2003 atomic mass evaluation, Nuclear Physics A 729, 337-676, 2003:*

$M(^{234}U) = 234.0409521 \pm 0.0000040$ g·mol^{-1}
$M(^{235}U) = 235.0439299 \pm 0.0000040$ g·mol^{-1}
$M(^{236}U) = 236.0455680 \pm 0.0000040$ g·mol^{-1}
$M(^{238}U) = 238.0507882 \pm 0.0000040$ g·mol^{-1}

[3)] The uncertainty is the expanded uncertainty with a coverage factor *k* = 2 corresponding to a level of confidence of about 95 % estimated in accordance with ISO/IEC Guide 98-3, Guide to the Expression of Uncertainty in Measurement (GUM:1995), ISO, 2008.

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Glossary

ANOVA	Analysis of variance
b	Slope in the equation of linear regression $y = a + bx$
CI	Confidence interval
CRM	Certified reference material
CLSI	Clinical and Laboratory Standards Institute
DS	Double spike
EC	European Commission
ERM®	Trademark of European Reference Materials
EU	European Union
GUM	Guide to the Expression of Uncertainty in Measurements [3]
GSMS	Gas Source Mass Spectrometry
IDMS	Isotope dilution mass spectrometry
IRMM	Institute for Reference Materials and Measurements of the JRC
ISO	International Organization for Standardization
IU	International units
JRC	Joint Research Centre of the European Commission
K-factor	Factor to correction mass fractionation in TIMS
k	Coverage factor
M	Molar mass
MCDS	Memory Corrected Double Standard method
MS	Mass spectrometry
$MS_{between}$	Mean of squares between-unit from an ANOVA
MSDS	Material safety data sheet
MS_{within}	Mean of squares within-unit from an ANOVA
MTE	Modified Total Evaporation
n	Number of replicates per unit
n(X)	Number of mole of the X species
N	Number of samples (units) analysed
n.a.	Not applicable
n.c.	Not calculated
QC	Quality control
rel	Index denoting relative figures (uncertainties etc.)
RM	Reference material
RSD	Relative standard deviation

RSE	Relative standard error (=RSD/$\sqrt{n}$)
r^2	Coefficient of determination of the linear regression
s	Standard deviation
s_{bb}	Between-unit standard deviation; an additional index "rel" is added when appropriate
$s_{between}$	Standard deviation between groups as obtained from ANOVA; an additional index "rel" is added as appropriate
SD	Standard deviation
se	Standard error
SEM	Secondary Electron Multiplier
SI	International System of Units
s_{meas}	Standard deviation of measurement data; an additional index "rel" is added as appropriate
s_{within}	Standard deviation within groups as obtained from ANOVA; an additional index "rel" is added as appropriate
s_{wb}	Within-unit standard deviation
T	Temperature
t	Time
$t_{\alpha, df}$	Critical t-value for a Student's t-test, with a level of confidence of 1-α and df degrees of freedom
TIMS	Thermal Ionisation Mass Spectrometry
t_{sl}	Proposed shelf life
u	standard uncertainty
U	expanded uncertainty
u^*_{bb}	Standard uncertainty related to a maximum between-unit inhomogeneity that could be hidden by method repeatability; an additional index "rel" is added as appropriate
u_{bb}	Standard uncertainty related to a possible between-unit inhomogeneity; an additional index "rel" is added as appropriate
u_{char}	Standard uncertainty of the material characterisation; an additional index "rel" is added as appropriate
u_{CRM}	Combined standard uncertainty of the certified value; an additional index "rel" is added as appropriate
U_{CRM}	Expanded uncertainty of the certified value; an additional index "rel" is added as appropriate
u_{Δ}	Combined standard uncertainty of measurement result and certified value
u_{lts}	Standard uncertainty of the long-term stability; an additional index "rel" is added as appropriate
u_{meas}	Standard measurement uncertainty
U_{meas}	Expanded measurement uncertainty

u_{rec}	Standard uncertainty related to possible between-unit inhomogeneity modelled as rectangular distribution; an additional index "rel" is added as appropriate
u_{sts}	Standard uncertainty of the short-term stability; an additional index "rel" is added as appropriate
VIM	Vocabulaire International de Métrologie – Concepts Fondamentaux et Généraux et Termes Associés (International Vocabulary of Metrology – Basic and General Concepts and Associated Terms) *[ISO/IEC Guide 99:2007]*
$\overline{y}$	Arithmetic mean
α	Significance level
Δ_{meas}	Absolute difference between mean measured value and the certified value
$\nu_{s,meas}$	Degrees of freedom for the determination of the standard deviation s_{meas}
$\nu_{MSwithin}$	Degrees of freedom of MS_{within}

1 Introduction

1.1 Background

The European Commission's Joint Research Centre, Institute for Reference Materials and Measurements (EC-JRC-IRMM) provides a wide range of certified reference materials, including nuclear CRMs to safeguards authorities and the nuclear industry. The IRMM-019 to IRMM-029 series of UF_6 isotope reference materials was originally certified between 1984 and 1996. At that time, the relative expanded uncertainties (k=2) were in the 0.05-0.2 % range for the major isotope amount ratio $n(^{235}U)/n(^{238}U)$ and between 0.3 % and 10 % for the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. Since the minor isotope amount ratios contain valuable information about the origin of the "feed" material used for commercial or possibly clandestine isotopic enrichment of UF_6, safeguards authorities now require accurate and reliable measurements and reference materials with smaller measurement uncertainties. The EC-JRC-IRMM therefore undertook the initiative to re-measure and certify this series particularly for minor isotope amount ratios in order to provide lower uncertainties on the certified values.

The certification of the isotope ratios for the IRMM-019 to IRMM-029 series in the 1980's-1990's was done in several procedural steps, involving uranium oxides (EC-171/031, /071, /194, /295, /446 series) which were fluorinated into UF_6 gas, then calibrated by GSMS (Gas Source Mass Spectrometry) against the UF_6 internal standards prepared by fluorination of gravimetric uranium oxide mixtures (Annex 1). The IRMM-183 to IRMM-187 series of certified uranium nitrate solutions was prepared from the original EC-171/031, /071, /194, /295, /446 series of uranium oxides as well, therefore the isotopic compositions are the same as the fluorinated fractions. The fluorinated fractions were used as calibrants for the certification of the IRMM-019 to IRMM-029 series.

The original certification project was a complicated process associated with uncertainties that were most likely underestimated. Furthermore, some of the fluorides prepared from the EC-171 series are exhausted and no longer available for GSMS measurements at IRMM.

Therefore it was decided to characterise the entire IRMM-019 to IRMM-029 series using a new set of calibrants in the form of uranium nitrate solutions gravimetrically prepared from certified reference materials, in combination with recently developed mass spectrometric measurement methods, in particular for Thermal Ionisation Mass Spectrometry (TIMS). This new series of UF_6 reference materials was characterised by IRMM to meet the requirements for reliable isotope reference materials for the accountancy measurements of UF_6 in compliance with the ITV-2010 values [4] for the major isotope amount ratios, and in addition is certified for the minor isotope amount ratios.

1.2 Choice of the material

In the 1980's-1990's, the certification measurements of the IRMM-019 to IRMM-029 series were performed by GSMS for the major isotope amount ratio $n(^{235}U)/n(^{238}U)$ using the IRMM-171/031 - IRMM-171/446 series of reference materials as calibrants, and by TIMS for the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. The IRMM-019 to IRMM-029 series covers the enrichment range from depleted uranium (IRMM-019 to IRMM-021) via natural uranium (IRMM-022) to enriched uranium (IRMM-023 to IRMM-029).

1.3 Design of the project

Certification measurements of IRMM-019 to IRMM-029 as well as homogeneity studies were performed using TIMS via a gas to solution conversion process.

After several steps of sample preparation including distillation from the batch ampoule to a single unit ampoule, hydrolysis of UF_6, nitration and dilution, the IRMM-019 to IRMM-029 series was analysed by TIMS (Triton, Thermo Fischer, Bremen, Germany) using the Modified Total Evaporation method (MTE) with IRMM-074/10 (Annex 2) isotope reference material as calibrant. The MTE method was introduced in 2003 in particular to determine the minor isotope amount ratios with smaller measurement uncertainties than those achieved by traditional methods [5, 6]. Additionally for some materials with low ^{236}U abundance, the major isotope amount ratios were measured by using the double spike (DS) IRMM-3636a (Annex 3), a mixture of highly enriched ^{233}U and ^{236}U with a ratio of $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})\approx 1$. This allows an internal mass fractionation correction and therefore leads to lower measurement uncertainties.

All TIMS measurements for this project were performed using a new set of calibrants which were recently certified reference materials:

1.) The IRMM-074 series of gravimetric mixtures is characterised by major isotope amount ratios $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ of about 1.00026 with uncertainties of 0.015 % (k=2) and isotope amount ratios $n(^{233}\mathrm{U})/n(^{235}\mathrm{U})$ ranging between 10^{-6} and 1, with uncertainties of 0.025 % (k=2) [7] (Annex 2). The IRMM-074 series was also used to assess the linearity of the secondary electron multiplier of the TIMS instrument and to determine the linearity correction parameter [7]. In addition, it was shown in [7], that the major isotope amount ratios $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ in IRMM-074 were confirmed by TIMS measurements using the major ratios of the predecessor series IRMM-072 as calibrant (similar isotope amount ratios [8, 9], prepared about 10 years earlier). Using IRMM-072, also the isotopic compositions of two further gravimetric mixtures, the IRMM-199 ($n(^{233}\mathrm{U})/n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$=1/1/1) and the NBL CRM U500 ($n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$=1/1), were confirmed at the same time [7]. This shows not only the 'consistency' of the gravimetrically prepared reference materials certified at IRMM, but also the link to the NBL U-series of reference materials. Nevertheless the most recently prepared CRM, the IRMM-074 was chosen as calibrant for all MTE measurements performed for this project.

2.) The IRMM-3636a "Double Spike" is a gravimetric mixture of ^{233}U and ^{236}U characterised by a ratio $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ of 1.01906 with an uncertainty of 0.016 % (k=2) [10, 11](Annex 3). The use of the IRMM-3636a "Double Spike" as a calibrant is advantageous for those materials of the IRMM-019 to IRMM-029 series which have rather low $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ ratios, because the "Double Spike" allows an internal rather than an external mass fractionation correction (see Section 6.1), and therefore leads to smaller uncertainties. It was shown in [10], that the ratio $n(^{233}\mathrm{U})/n(^{236}\mathrm{U})$ of IRMM-3636a was confirmed by TIMS measurements using the major isotope amount ratio of IRMM-074/10 of the series IRMM-074 as calibrant, the same used for all MTE measurements in this project.

3.) The IRMM-075 series (Annex 4) of gravimetric mixtures is characterised by major isotope amount ratios $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ of about 0.007256 (close to natural uranium) with uncertainties of 0.05 % (k=2) and certified isotope amount ratios $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ ranging between 10^{-9} and 10^{-4}, with uncertainties varying between 0.037 % and 0.63 % (k=2) [12]. This series was not used as calibrant, but for measurement quality control, in particular for measurements of the $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ isotope amount ratios of the IRMM-019 to IRMM-029 series in a wide dynamic range and using different types of detectors such as Faraday cups and a secondary electron multiplier (SEM) in combination with an energy filter to improve the abundance sensitivity.

The results of all certification measurements for the IRMM-019 to IRMM-029 series were confirmed using the recently installed "Uranus" (Thermo Fischer, Bremen, Germany) UF_6 Gas Source Mass Spectrometer, for both major and minor isotope amount ratios [13].

IRMM has been providing IRMM-019 to IRMM-029 series for more than 20 years. On customer requests, gases are distilled from one of the batch ampoules under vacuum into a single unit monel (copper-nickel alloy) ampoule. After this preparation step each ampoule is verified by GSMS. IRMM has therefore an on-going database of measurement values which is used in this certification project to evaluate the long-term stability (see paragraph 5).

2 Participants

Project management and evaluation, processing, homogeneity study, stability study and characterisation were performed at the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), Geel, Belgium. IRMM participates regularly in several uranium interlaboratory comparisons on uranium oxides and UF_6 materials organised by the French "Commissariat à l'Energie Atomique et aux Energies Alternatives" (CEA) / "Commission d'établissement des méthodes d'analyses" (CETAMA) and the US "Department of Energy (DOE) / New Brunswick Laboratory (NBL)". The IRMM is accredited for ISO 17025. There were no further participants or other laboratories involved in this certification project.

3 Material processing and process control

3.1 Origin of the starting material

The IRMM-019 to IRMM-029 series was prepared at the European Commission, Joint Research Centre, Institute for Reference Materials and Measurements (IRMM), in the 1980's -1990's. They are stored in monel ampoules at the IRMM.

3.2 Processing

Each sample of the IRMM-019 to IRMM-029 materials is prepared by distilling UF_6 from a 'mother' ampoule of the respective material into a 'daughter' ampoule.

A clean monel ('daughter') ampoule is assembled, evacuated and a leak test is performed using the leak detector Leybold UL 200 (Leybold, Greentown,USA). The empty ampoule is weighed.

The ampoule is connected to a distillation line and cooled at -196 ^{0}C using liquid nitrogen. On the input of the distillation line the mother ampoule containing the reference material is connected (Figure 1). UF_6 gas is distilled under vacuum from the mother ampoule into the daughter ampoule. The distillation time is estimated according to the quantity of material to be distilled. The gas is cleaned, i.e. purified from components more volatile than UF_6, by cooling the ampoule in liquid nitrogen and opening and evacuating the ampoule under high vacuum ($<3\times10^{-6}$ mbar). The ampoule is then closed under vacuum, disconnected from the distillation line and weighed. If the transferred mass of UF_6 is too small, the ampoule has to be reconnected in order to repeat the distillation process, for this purpose the distilled quantity, distillation speed and the remaining time have to be estimated. Once the required quantity (depending on customer request or the intended use) is reached, the ampoule is closed under vacuum and disconnected from the line. The UF_6 in the ampoule is homogenised by heating in a special oven for at least 1 h at 150 °C. For this project, about 22 g of UF_6 were distilled in monel ampoules: 20 g foreseen for later distribution or post-certification monitoring, 1 g converted for characterisation measurements by TIMS, and another 1 g used for verification measurements by GSMS.

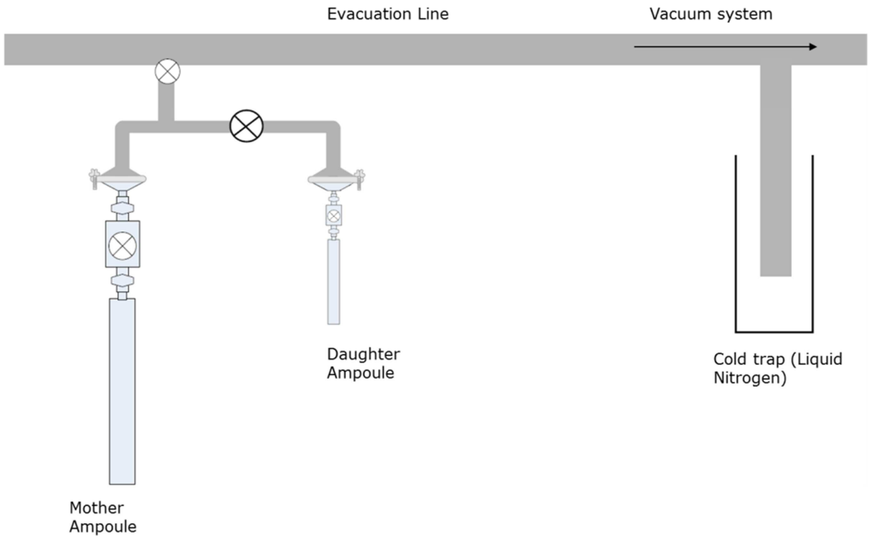

Figure 1 : Distillation scheme

For certification and homogeneity measurements by TIMS, a fraction of about 1 g of UF_6 from each monel ampoule was converted into a uranium nitrate solution. The ampoule was therefore connected to a distillation line. On the output side, a cleaned glass ampoule was connected and cooled with liquid nitrogen. A distillation was performed from the monel ampoule to the glass ampoule in order to transfer a small quantity of UF_6. The cooled glass ampoule was disconnected from the line and deionised water (18.2 MΩ·cm) added to hydrolyse the UF_6 gas. The obtained solution was transferred to a weighted beaker and the glass ampoule was rinsed several times. The solution was evaporated to dryness on a hotplate under a fume hood. Suprapur® nitric acid (65%, Merck, Darmstadt, Germany) was subsequently added in order to dissolve and convert the uranium into nitrate form ($UO_2(NO_3)_2 \cdot 6H_2O$). The acid was evaporated to dryness on the hot plate. The nitration process was repeated twice. The dried uranium nitrate was eventually dissolved using nitric acid with a concentration of 1 $mol \cdot L^{-1}$, prepared with Suprapur® nitric acid and deionised water in order to obtain the required uranium concentration of 2 $\mu g \cdot \mu L^{-1}$ for TIMS measurements.

3.3 Process control

Ampoules are checked for leakage before and during the distillation process. The mass of the distilled uranium hexafluoride is controlled.

Prior to distribution of any IRMM UF_6 reference materials, a verification measurement by Gas Source Mass Spectrometry (GSMS) is performed in order to verify that the gas contained in the monel ampoule has the same isotope composition as the gas contained in the mother ampoule. Before the GSMS analysis, an additional conditioning process is performed by cooling the ampoule at -78 °C with a dry ice-ethanol mixture and evacuating the volatile impurities under vacuum (pressure below 1×10^{-2} mbar).

In addition to the certification and homogeneity measurements, two blank solutions were prepared (blank hydrolysis following by nitration and dilution steps) and analysed by TIMS in order to check for any possible (natural uranium) contamination.

4 Homogeneity

A key requirement for any reference material is the equivalence between the various units. In this respect, it is relevant whether the variation between units is significant compared to the uncertainty of the certified value. In contrast, it is not relevant if the variation between units is significant compared to the analytical variation. Consequently, ISO Guide 34 requires RM producers to quantify the between-unit variation. This aspect is covered in between-unit homogeneity studies.

The within-unit inhomogeneity does not influence the uncertainty of the certified value when the minimum sample intake is respected, but determines the minimum size of an aliquot that is representative for the whole unit.

4.1 Between-unit homogeneity

The between-unit homogeneity was evaluated to ensure that the certified values of the CRM are valid for all units of the material, within the stated uncertainty.

For this project, it has to be taken into consideration, that:

i) For some reference materials of the IRMM-019 to IRMM-029 series, there is insufficient quantity available to perform a meaningful homogeneity study,

ii) The ampoules are systematically verified by GSMS for each customer request in order to exclude any inhomogeneity and confirm the agreement between the mother ampoule and the daughter ampoule. This basically constitutes the required homogeneity testing (according to ISO Guide 35:2006). Nevertheless, a homogeneity study was performed.

The homogeneity was investigated using only one of the CRMs, namely IRMM-023, with the intention to extrapolate the homogeneity testing results from IRMM-023 to all other reference materials (see explanations below).

For the homogeneity testing, from each of the 6 ampoules containing 22 g of this material about 1 g was distilled and converted into nitrate solution. Additionally one sample was prepared directly from the IRMM-023 mother ampoule.

The six solutions of IRMM-023 were analysed by TIMS by two methods, firstly utilising the Double Spike (DS) method using IRMM-3636a ($n(^{233}U)/n(^{236}U) \approx 1/1$) for measuring the major isotope amount ratio $n(^{235}U)/n(^{238}U)$ with the best possible precision and lowest measurement uncertainty, and secondly utilising the Modified Total Evaporation (MTE) method. For MTE measurements, the ^{234}U was measured using a Faraday cup (connected to an amplifier with a $10^{12}\ \Omega$ resistor), and the ^{236}U using the secondary electron multiplier (SEM). The use of an amplifier with a $10^{12}\ \Omega$ resistor compared to a 'standard' $10^{11}\ \Omega$ resistor has the advantage of improving the signal-to-noise ratio by a factor of about two [6].

Each unit (solution) was measured in three replicates for the DS method using IRMM-3636a (mixed on the same filament) and in four replicates for the MTE method together with several (at least five) replicates of the certified reference material IRMM-074/10 to correct for the mass fractionation effects. All DS-measurements were performed on the same TIMS sample turret under repeatability conditions. For MTE, this is not possible due to the limited number of positions on a TIMS sample turret, therefore four independent samples were measured on the same TIMS sample turret on the same day (3 solutions from different ampoules and the solution from the mother ampoule); therefore, the MTE-measurements for all six samples of IRMM-023 were performed under intermediate precision conditions rather than repeatability conditions. However an ANOVA-study on the solution from the mother ampoule showed that there was no observable turret to turret variation.

The respective replicates of samples were measured in a randomised manner in order to separate any potential analytical drift from a trend in the preparation (distillation) sequence.

Regression analyses were performed to evaluate potential trends in the analytical sequence as well as trends in the preparation (distillation) sequence. No trends in the preparation sequence were observed. For DS measurements, some significant (95 % confidence level) trends in the analytical sequence were visible (see Annex 5). The correction of bias, even if they are statistically insignificant, was found to combine the smallest uncertainty with the highest probability to cover the true value [14]. Correction of trends is therefore expected to improve the sensitivity of the subsequent statistical analysis through a reduction in analytical variation without masking potential between-unit heterogeneities. As the analytical sequence and the unit numbers were not correlated, trends significant on at least a 95 % confidence level were corrected as shown below:

$$corrected\ result = measured\ \ result - b \cdot i \qquad \textbf{Equation 1}$$

b **=** slope of the linear regression

i **=** position of the result in the analytical sequence

The trend-corrected dataset was tested for consistency using Grubbs outlier tests on a confidence level of 99 % on the individual results and the unit means. Some outlying individual results were detected. Since no technical reason for the outliers could be found, all the data were retained for statistical analysis.

Quantification of between-unit inhomogeneity was accomplished by analysis of variance (ANOVA), which can separate the between-unit variation (s_{bb}) from the within-unit variation (s_{wb}). The latter is equivalent to the method repeatability if the individual samples are representative for the whole unit.

Evaluation by ANOVA requires unit means which follow at least a unimodal distribution and results for each unit that follow unimodal distributions with approximately the same standard deviations. Distribution of the unit means was visually tested using histograms and normal probability plots. Too few data are available for the unit means to make a clear statement of the distribution. Therefore, it was visually checked whether all individual data follow a unimodal distribution using histograms and normal probability plots. Minor deviations from unimodality of the individual values do not significantly affect the estimate of between-unit standard deviations. The results of all statistical evaluations are given in Table 1.

Table 1: Results of the statistical evaluation of the homogeneity studies

Isotope amount ratio (TIMS)	Trends[1] (before correction)		Outliers[2]		Distribution	
	Analytical sequence	Filling sequence	Individual results	Unit means	Individual results	Unit means
MTE-$n(^{234}U)/n(^{238}U)$	no	no	1–technical reason[3] (removed)	none	normal	normal
MTE-$n(^{235}U)/n(^{238}U)$	no	no	1–technical reason[3] (removed)	none	normal	normal
DS-$n(^{235}U)/n(^{238}U)$	yes	no	1–technical reason[3] (removed) 1–statistical reason (retained)	none	normal	normal
MTE-$n(^{236}U)/n(^{238}U)$	no	no	1–technical reason[3] (removed) 1–statistical reason (retained)	yes	normal	normal

[1] at 95 % confidence level

[2] at 99 % confidence level

[3] Technical reasons occurred during the measurements. These can have different origins such as no sufficient collected signal, bad instrument settings, and recurring problems during the run.

One has to bear in mind that $s_{bb,rel}$ and $s_{wb,rel}$ are estimates of the true standard deviations and therefore subject to random fluctuations. Therefore, the mean square between groups ($MS_{between}$) can be smaller than the mean squares within groups (MS_{within}), resulting in negative arguments under the square root used for the estimation of the between-unit variation, whereas the true variation cannot be lower than zero. In this case, u^*_{bb}, the maximum inhomogeneity that could be hidden by method repeatability, was calculated as described by Linsinger *et al.* [15]. The calculated value of u^*_{bb} was comparable to the limit of detection of an analytical method, yielding the maximum inhomogeneity that might be undetected by the given study setup.

Method repeatability ($s_{wb,rel}$), between–unit standard deviation ($s_{bb,rel}$) and $u^*_{bb,rel}$ were calculated as:

$$s_{wb,rel} = \frac{\sqrt{MS_{within}}}{\bar{y}} \qquad \textbf{Equation 2}$$

$$s_{bb,rel} = \frac{\sqrt{\frac{MS_{between} - MS_{within}}{n}}}{\bar{y}} \qquad \textbf{Equation 3}$$

$$u^*_{bb,rel} = \frac{\sqrt{\frac{MS_{within}}{n}}\sqrt[4]{\frac{2}{\nu_{MSwithin}}}}{\bar{y}} \qquad \textbf{Equation 4}$$

MS_{within}	mean square within a unit from an ANOVA
$MS_{between}$	mean squares between-unit from an ANOVA
$\bar{y}$	mean of all results of the homogeneity study
n	mean number of replicates per unit
$\nu_{MSwithin}$	degrees of freedom of MS_{within}

However, a different approach was adopted for the analyte for which 1 outlying unit means was detected. In this case between-unit inhomogeneity was modelled as a rectangular distribution limited by the largest outlying unit mean, and the rectangular standard uncertainty of homogeneity was estimated by:

$$u_{rec} = \frac{\left|outlier - \bar{y}\right|}{\sqrt{3} \cdot \bar{y}} \qquad \textbf{Equation 5}$$

$\bar{y}$	mean of all results of the homogeneity study

It should be mentioned that the outlying unit means are a result of presence of outlying individual values and do not necessarily reflect a real inhomogeneity in the isotopic composition.

Table 2: Results of the homogeneity study on IRMM-023

Measurand-Method	$s_{wb,rel}$ [1)] [%]	$s_{bb,rel}$ [1)] [%]	$u^*_{bb,rel}$ [1)] [%]	$u_{rec,rel}$ [1)] [%]	$u_{bb,rel}$ [1)] [%]
$n(^{234}U)/n(^{238}U)$-MTE	0.0213 %	0.0105 %	0.0064 %	n.a.	0.0105 %
$n(^{235}U)/n(^{238}U)$-MTE	0.0125 %	n.c.	0.0038 %	n.a.	0.0038 %
$n(^{235}U)/n(^{238}U)$-DS	0.0026 %	0.0013 %	0.0010 %	n.a.	0.0013 %
$n(^{236}U)/n(^{238}U)$-MTE	n.a.	n.a.	n.a.	0.67 %	0.67 %

n.c.: cannot be calculated as $MS_{between} < MS_{within}$

n.a.: not applicable

1) Rounding rules not applicable to intermediate results

For the isotope amount ratios where the homogeneity study showed no outlying unit means or trends in the preparation sequence, the between-unit standard deviation can be used as estimate of u_{bb}. As u^*_{bb} sets the limits of the study to detect inhomogeneity, the larger value of s_{bb} and u^*_{bb} is adopted as uncertainty contribution to account for potential inhomogeneity.

One outlying unit mean was found for one isotope amount ratio. However, taking this extreme value into account, the inhomogeneity quantified as u_{rec} is still sufficiently small to make the material useful. Therefore, u_{rec} was used as an estimate of u_{bb}.

As stated previously, the between-unit homogeneity was investigated for only one of the materials to be certified, namely IRMM-023, so the results of this homogeneity study can be directly used for the calculation of the uncertainty of the certified values of IRMM-023. Nevertheless for the final uncertainty calculation of all other materials of the IRMM-019 - IRMM-029 series, reasonable extrapolations from the between-unit homogeneity results of IRMM-023, i.e. the uncertainty contribution to account for potential inhomogeneity, were applied.

Firstly, for measurements of the major isotope amount ratios $n(^{235}U)/n(^{238}U)$ two methods were used during the characterisation: MTE and DS method. For both methods, it has been reported in [5, 6, 11,16], that the relative standard deviation (RSD) of measurement results on the same sample turret is independent of the value of the ratio itself.

Looking at the *relative* standard deviations (RSD) of the measurement results observed during the characterisation in Figure 2 and Figure 3, the predictions of having ratio-independent RSDs were also confirmed by our measurements for the full range of ratios values of the IRMM-019 - IRMM-029 series.

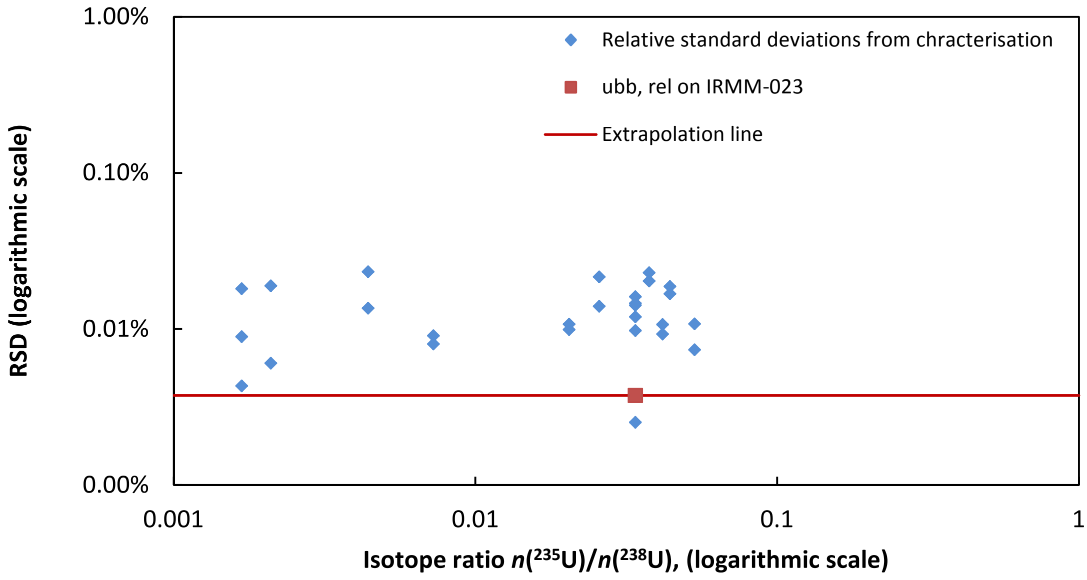

Figure 2: Relative standard deviations (RSD) for $n(^{235}U)/n(^{238}U)$-MTE during characterisation, the result from homogeneity test (see Table 2) and its extrapolation.

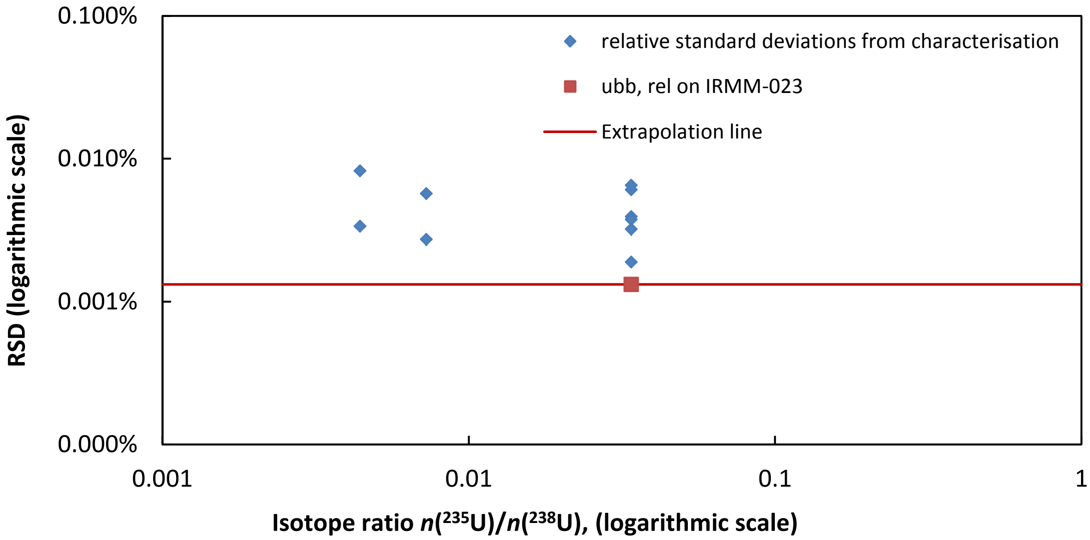

Figure 3: Relative standard deviations (RSD) for $n(^{235}U)/n(^{238}U)$-DS during characterisation, the result from homogeneity test (see Table 2) and its extrapolation.

The calculated u_{bb} for IRMM-023 was found to be even below the RSDs observed during characterisation measurements. The homogeneity testing therefore did not show any significant between-bottle inhomogeneity, so the results for the relative u_{bb} can be extrapolated using the method-characteristic "trend" of the RSD to all other ratios and materials. For the two methods, this means that the extrapolated (in this case constant) relative values of u_{bb} for these methods will be applied for the uncertainty calculations of all materials to be certified.

For the measurements of the minor isotope amount ratios, the situation is slightly different due to the different analytical characteristics of the methods used.

This applies for instance for measurements of the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ using the SEM as detector for the isotopes ^{234}U and ^{236}U during characterisation measurements. As previously, the RSDs observed during the characterisation are plotted versus the isotope amount ratio (Figure 4). In this case the dependency of the RSD on the isotope amount ratio value is obvious. This is due to counting statistics (Poisson statistics), which means that an increase (decrease) of a factor of 10 of the count rate for the isotope measured on the SEM causes a decrease (increase) of the RSD by a factor of √10, as also described in [5, 6]. This dependency is represented by a line in a double-logarithmic plot of the RSD versus the isotope amount ratio in Figure 4. The $u_{bb,rel}$ determined for IRMM-023 was found to be consistent with the RSDs observed during characterisation measurements of all materials. The relative u_{bb} determined for IRMM-023 is extrapolated using the method-characteristic dependency given by the counting statistics to all other ratios and materials. For calculating the final measurement uncertainties of the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ using the SEM, this means, that the extrapolated values of u_{bb} given by the red line in Figure 4 will be applied for this method.

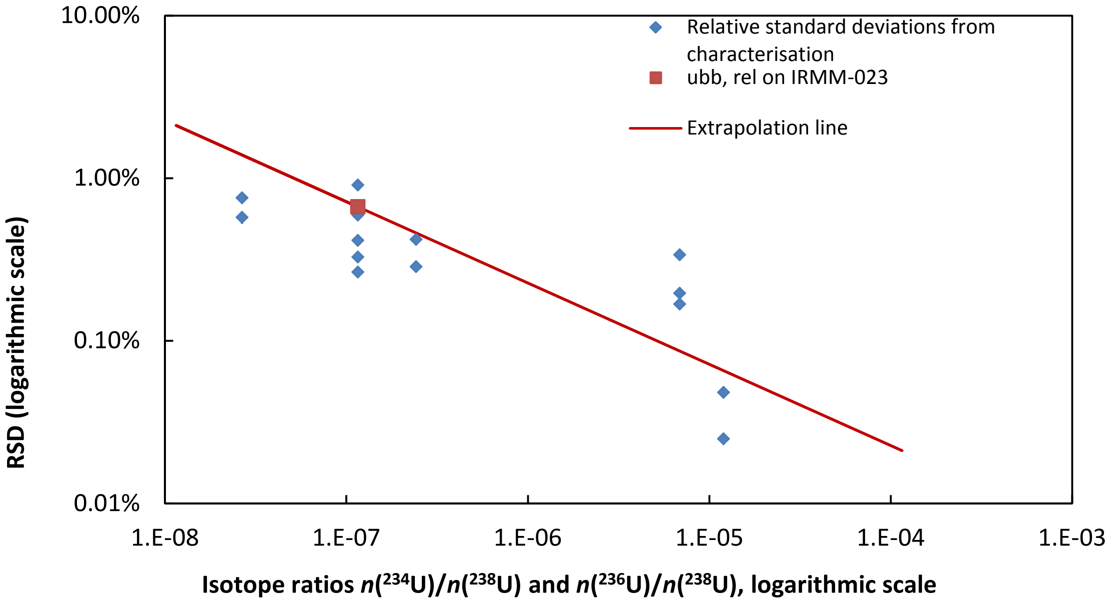

Figure 4: Relative standard deviations (RSD) for $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ using the SEM for ^{234}U and ^{236}U during characterisation measurements, the result from homogeneity test (see Table 2) and its extrapolation according to counting statistics [5, 6]

For the measurements of the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ using Faraday cups (equipped with a 10^{12} Ω resistor), the situation is different. In this case not the relative, but the *absolute* standard deviations are independent of the ratio values for the applied range of intensities (Figure 5), because they are mainly given by the Faraday cup amplifier noise, also known as Johnson noise [17]. The u_{bb} calculated for IRMM-023 is also dominated by this phenomenon. As a consequence, for measuring $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ using Faraday cups this means that the extrapolated absolute (constant) value of u_{bb} (see red line in Figure 5) for this method is be applied for the uncertainty calculations of all materials to be certified.

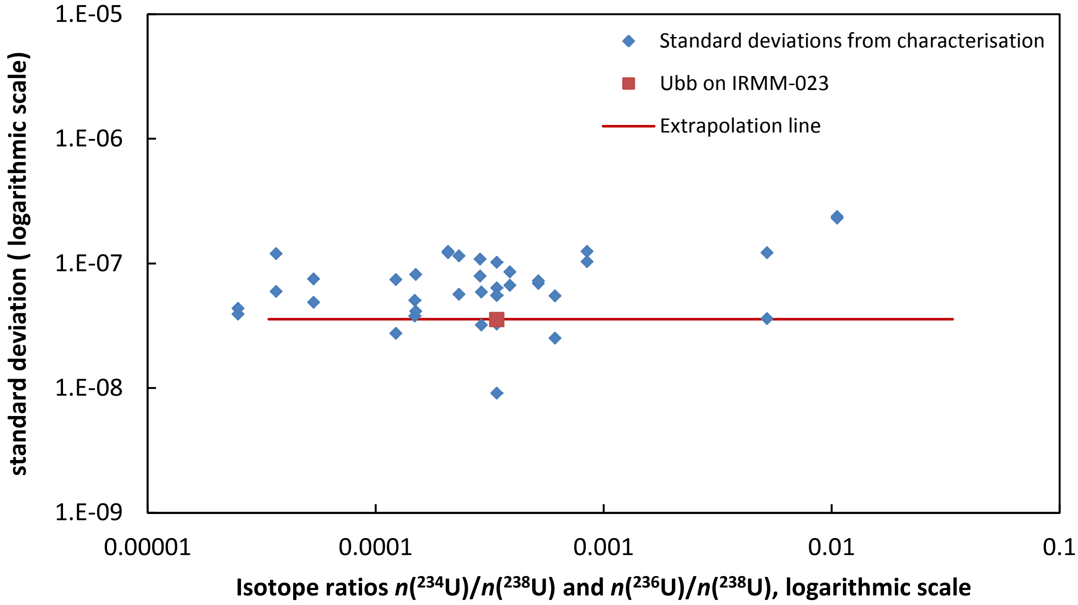

Figure 5: Absolute standard deviations (SD) for $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{236}\text{U})/n(^{238}\text{U})$ using the Faraday Cups ($10^{12}\Omega$) for ^{234}U and ^{236}U during characterisation measurements, the result from homogeneity test (Table 2) and its extrapolation according to Johnson noise [17].

In conclusion, the uncertainty contributions from the homogeneity testing are found to be at the same level (or below) as the standard deviations of measurements results encountered during the characterisation measurements (Figures 2-5 above). This is due to the fact that there is no significant between-unit inhomogeneity. Therefore, the uncertainty contributions calculated from the homogeneity testing can be extrapolated considering the known measurement characteristics published in the literature [5, 6, 11 16]. The method of extrapolation depends on the particular isotope amount ratio and on the measurement method used. Following this study the values for homogeneity contribution are summarized below.

Table 3: Results of the homogeneity study for each materials

Materials/ isotope amount ratios	$u_{\text{bb, rel}}$ 1) [%]	Materials/ isotope amount ratios	$u_{\text{bb, rel}}$ 1) [%]
IRMM-019		IRMM-025	
$n(^{234}\text{U})/n(^{238}\text{U})$	0.087	$n(^{234}\text{U})/n(^{238}\text{U})$	0.029
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038	$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038
$n(^{236}\text{U})/n(^{238}\text{U})$	0.098	$n(^{236}\text{U})/n(^{238}\text{U})$	0.024
IRMM-020		IRMM-026	
$n(^{234}\text{U})/n(^{238}\text{U})$	0.066	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0024
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038	$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038
$n(^{236}\text{U})/n(^{238}\text{U})$	0.012	$n(^{236}\text{U})/n(^{238}\text{U})$	0.017
IRMM-021		IRMM-027	
$n(^{234}\text{U})/n(^{238}\text{U})$	0.143	$n(^{234}\text{U})/n(^{238}\text{U})$	0.015
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0013	$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038
$n(^{236}\text{U})/n(^{238}\text{U})$	1.39	$n(^{236}\text{U})/n(^{238}\text{U})$	0.0092

IRMM-022		IRMM-028	
$n(^{234}\text{U})/n(^{238}\text{U})$	0.067	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0058
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0013	$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038
$n(^{236}\text{U})/n(^{238}\text{U})$	0.46	$n(^{236}\text{U})/n(^{238}\text{U})$	0.00069
IRMM-023		IRMM-029	
$n(^{234}\text{U})/n(^{238}\text{U})$	0.0105	$n(^{234}\text{U})/n(^{238}\text{U})$	0.0042
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0013	$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038
$n(^{236}\text{U})/n(^{238}\text{U})$	0.67	$n(^{236}\text{U})/n(^{238}\text{U})$	0.00034
IRMM-024			
$n(^{234}\text{U})/n(^{238}\text{U})$	0.012		
$n(^{235}\text{U})/n(^{238}\text{U})$	0.0038		
$n(^{236}\text{U})/n(^{238}\text{U})$	0.0069		

[1)] Rounding rules not applicable to intermediate results

4.2 Within-unit homogeneity and minimum sample intake

The within-unit homogeneity is closely correlated to the minimum sample intake. Due to this correlation, individual aliquots of a material may not contain the same amount of analyte. The minimum sample intake is the minimum amount of sample that is representative for the whole unit and thus can be used in an analysis. Sample sizes equal or above the minimum sample intake guarantee the certified value within its stated uncertainty.

Homogenisation was done during the CRM production on the mother ampoule in the 1980's-1990's and several measurements of the isotope amount ratios were performed in order to check the within-unit homogeneity [18]. Additionally a homogenisation step is realised on the daughter ampoule after the distillation. Therefore the released gas from the daughter ampoule is homogeneous and there is no "minimum sample intake" to be taken into consideration for the user.

5 Stability

Stability testing is necessary to establish conditions for storage (long-term stability) as well as conditions for dispatch to the customers (short-term stability). During transport, especially in summer time, temperatures up to 60 °C could be reached and stability under these conditions must be demonstrated if transport at ambient temperature will be applied.

5.1 Short-term stability study

The IRMM-019 to IRMM-029 series consists of uranium hexafluoride isotopic reference materials contained in monel (copper nickel alloy) ampoules closed under vacuum condition. Since the isotopic composition is independent on the temperature, there is no impact from transportation on the uranium isotopic composition. Therefore no short term stability study was performed and the materials can be dispatched without further precautions under ambient conditions.

5.2 Long-term stability study

Long term study was carried out in two complimentary steps using historical data coming for IRMM-023 stored at room temperature:

1. In 2009 measurements were performed on IRMM-023 by TIMS using the double spike (DS) technique (for more details see Section 6) on several samples of freshly distilled UF_6, converted into uranyl nitrate solution. The data showed that the certified major

isotope amount ratio $n(^{235}U)/n(^{238}U)$ did not change significantly between 2009 and 2013, covering a period of four years. However, since these measurements were not performed on regular basis, it is not considered meaningful to use them for the long term stability study (Figure 6).

2. The long term stability itself is realised using historical data from verification measurements by GSMS which were performed on numerous ('daughter') ampoules prior to sale. These verification measurements of the daughter ampoules were done relative to the mother ampoule without the use of a reference material (Figure 7).

For step 1, the IRMM-023 data collected in 2009 by TIMS using the double spike method were combined with the data measured for the characterisation in the frame of this project, as shown in Figure 6.

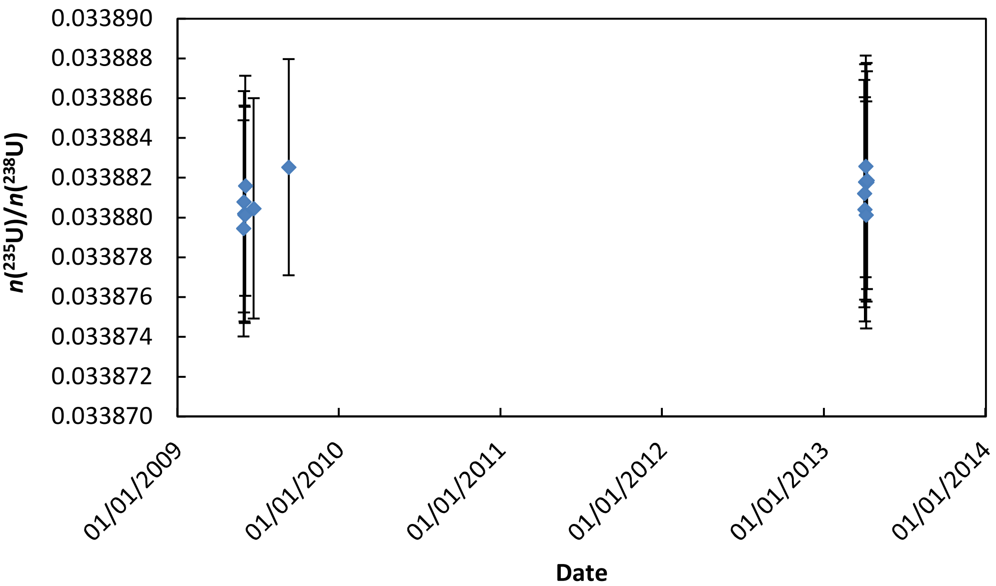

Figure 6: TIMS-DS measurements (*n*=14) on IRMM-023 performed between 2009 and 2013. Uncertainties are given with a coverage factor of *k*=2.

The measurement results were screened for outliers using the single and double Grubbs test at 99% confidence level. No outliers were detected and all data were therefore retained for statistical analysis. Furthermore, the data were plotted against measurement date and linear regression lines of isotope amount ratio versus time were calculated. The slope of the regression lines was tested for statistical significance. The slope was not significantly different from zero (on 95 % confidence level) for 18 °C. No technically unexplained outliers were observed at 99 % confidence level and none of the trends was statistically significant at the 95 % confidence level. This study showed therefore that there is no significant variation between 2009 and 2013 on the major isotope amount ratio in the mother ampoule of IRMM-023.

Nevertheless, the long term stability study was performed using the data coming from GSMS (step 2) (Figure 7). Indeed, during more than 30 years (from 1989 to 2010), monel ampoules containing UF_6 were analysed using the MAT511 GSMS in order to verify that after each distillation process, the gas in the daughter ampoule (usually for a customer) has the same isotopic composition as the gas contained in the reference ampoule. Alpha values were calculated as the ratio of the $n(^{235}U)/n(^{238}U)$ isotope amount ratio of the daughter ampoule to the $n(^{235}U)/n(^{238}U)$ isotope amount ratio of the mother ampoule. The isotope amount ratios of the daughter ampoule can be deduced from the recorded alpha-values by multiplication with the certified value. For this reference material a sufficient number of data was collected over the last 30 years (Figure 7).

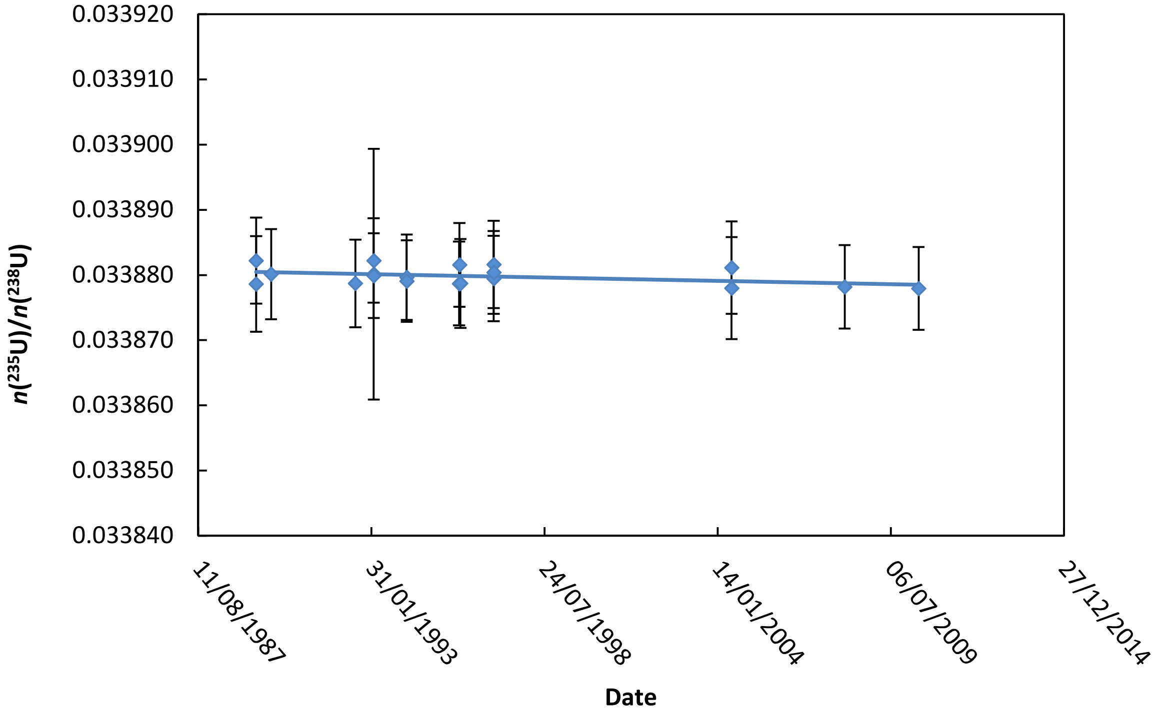

Figure 7: Deduced $n(^{235}\text{U})/n(^{238}\text{U})$ from 1989 to 2011. (Uncertainties are represented with a coverage factor of k=2).

Similarly to the TIMS measurements, the results were screened for outliers using the single and double Grubbs tests. No outliers were detected at 99% confidence level and all data were therefore retained for statistical analysis. Furthermore, the data were plotted against storage time and linear regression lines of isotope amount ratio versus time were calculated. The slope of the regression lines was tested for statistical significance (loss/increase due to storage conditions). The slope of the regression lines was not significantly different from zero (on 95 % confidence level) for room temperature. No technically unexplained outliers were observed at 99 % confidence level and none of the trends was statistically significant on a 95 % confidence level. The material can therefore be stored at room temperature.

5.3 Estimation of uncertainties

Due to the intrinsic variation of measurement results, no study can rule out degradation of materials completely, even in the absence of statistically significant trends. It is therefore necessary to quantify the potential degradation that could be hidden by the method repeatability, i.e. to estimate the uncertainty of stability. This means, even under ideal conditions, the outcome of a stability study can only be "degradation is 0 ± x % per time".

Uncertainties of stability during storage were estimated as described in [19]. For this approach, the uncertainty of the linear regression line with a slope of zero was calculated. The uncertainty contributions u_{lts} were calculated as the product of the chosen shelf life and the uncertainty of the regression lines as:

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum (x_i - \bar{x})^2}} \cdot t_{sl}$$ **Equation 6**

RSD	relative standard deviation of all results of the stability study
x_i	result at time point *i*
$\bar{x}$	mean results for all time points
t_{sl}	chosen shelf life (10 years at 18 ºC)

The calculated u_{lts} on GSMS results demonstrates that the storage contribution is negligible compared to the characterisation and homogeneity (u_{lts} =0.000044% for 10 years) for the major isotope ratio $n(^{235}U)/n(^{238}U)$.

Concerning the minor isotope amount ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$, it is known that all uranium isotopes have the same physical properties, except for radioactive decay and mass fractionation effect :

1.) The half-lifes of the isotopes ^{234}U, ^{235}U, ^{236}U and ^{238}U (respectively 245.5×10^3 a, 704×10^6 a, 23.42×10^6 a and 4.47×10^9 a [20] are significantly longer than the shelf life of 10 years.

2.) No effect was shown on the isotope amount ratio $n(^{235}U)/n(^{238}U)$ for long term stability.

3.) The homogeneity study has shown that there is no change of the isotopic composition by the distillation process, because the isotopic composition of the material converted from the mother ampoule (of IRMM-023) is found to be the same as the material converted from any of the daughter ampoules prepared by (an additional) distillation from the mother ampoule. This proves that there were no observable fractionation effects during the distillation processes performed for this long term stability study. Therefore, also the minor isotope amount ratios in the reference ampoule cannot have altered due to any fractionation effects over the period of the long term stability study.

It can be concluded that the stability effects are negligible for both major and minor isotope amount ratios. This is applicable to all the other UF_6 materials of the IRMM-019 to IRMM-029 series as well.

6 Characterisation

The material characterisation is the process of determining the property values of a reference material. The material characterisation was based on a primary method of measurement, confirmed by an independent method. A primary method of measurement (also called "primary reference method" in the International Vocabulary of Metrology (VIM) [21]) is a method that does not require calibration with a standard of the same measurand and does not depend on a chemical reaction. Such methods are of highest metrological order and often yield results with low uncertainties. However, it is nevertheless prudent to demonstrate absence of bias or gross errors by using an independent method of lower metrological order. For all methods used for the characterisation for reference materials IRMM-019 to 029 series by TIMS, such as the MTE and DS methods (see chapter 1.3), synthetic reference materials in the form of uranium nitrate solution were used as calibrants. These reference materials were prepared by gravimetrically mixing purified oxides or nitrate solutions of highly (>99.96%) enriched ^{233}U, ^{235}U, ^{236}U and ^{238}U starting materials. The certified values for their isotope amount ratios are directly traceable via mass determinations (using substitution weighing) to the SI, the certified values were not obtained (but only verified) by mass spectrometry measurements. Therefore this methodology can be considered equivalent to a primary reference method.

6.1 Methods used

For each material, two daughter ampoules were independently distilled from a mother ampoule, converted into nitrate solutions and diluted to a uranium concentration of 2 µg/µL. Measurements were performed by TIMS. Depending on the isotopic composition different methods were applied:

- For materials with expected $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ ratios above 2×10^{-5}, the Modified Total Evaporation (MTE) method with Faraday cups as detectors is used. The Faraday cups collecting the major isotopes (^{235}U, ^{238}U) are connected to amplifiers equipped with 10^{11} Ω resistors. The Faraday cups collecting the minor isotopes are connected to amplifiers equipped with 10^{12} Ω resistors. The MTE method and the calculations are explained in [5, 6]. For this method, six TIMS-filaments were loaded with 4 µg of uranium for each solution. Additionally, six replicates of a certified reference material (IRMM-074/10) and three replicates of another CRM used as quality control sample (QC sample) were measured on the same TIMS sample turret.

- For the materials with an expected ratio above 2×10^{-5} for the $n(^{234}U)/n(^{238}U)$ ratio and below 2×10^{-5} for the $n(^{236}U)/n(^{238}U)$ ratio, two complimentary methods were used:

i) The minor isotope amount ratios are measured by MTE. In this case the ^{234}U was measured with the 10^{12} Ω amplifier connected to a Faraday cup. The ^{236}U is measured with the ion counter (SEM). The ^{234}U was also measured with the SEM in order to determine the intercalibration factor between the Faraday cups and the ion counter (see [5, 6] for more details). For this method, five TIMS-filaments were loaded with 4 µg of uranium for each solution. Additionally, six replicates of a certified reference material (IRMM-074/10) and three replicates of each QC sample were included.

ii) As these materials have low $n(^{236}U)/n(^{238}U)$ ratios, another method has been used in addition to MTE in order to characterise the major isotope amount ratio with a smaller measurement uncertainty. This method is called the Double Spike method [11]. Prior to the measurements each replicate sample containing 4 µg of uranium was loaded on the same filament together with 100 ng of a double spike reference material IRMM-3636a. The IRMM-3636a "Double Spike" (DS) is a gravimetric mixture of ^{233}U and ^{236}U characterised by an isotope amount ratio $n(^{233}U)/n(^{236}U)$ of 1.01906 with an expanded uncertainty of 0.016% (k=2, Annex 3). The "Double Spike" allows an internal rather than an external mass fractionation correction [10], leading to better repeatability for the measurements and as consequence lower measurement uncertainties. Four replicates of each daughter ampoule and five replicates of the quality control sample were measured.

- For materials with an expected abundance below 2×10^{-5} for ^{234}U and above 2×10^{-5} for ^{236}U, the 'classical' MTE does not allow the measurements of the ^{234}U isotope with the SEM. A new method, the so called "reverse-MTE", had therefore been developed. This method is similar to MTE (same principle, same filament heating script, similar calculations) but in this case allows the measurements of the ^{234}U isotope on the ion counter, which is then cross-calibrated using the ^{236}U ion beam. For each solution of a material, five TIMS-filaments were loaded with 6 µg of uranium. Additionally, six replicates of a reference material (IRMM-074/10) and three replicates of each quality control sample were added to the sample turret.

For IRMM-023, the results measured for the homogeneity study were used for the characterisation exercise (see Section 4).

Blank solutions (water and acid coming from sample preparation without addition of uranium) were also checked by adding the ^{233}U spike reference material IRMM-058 (Annex 6) and analysed by IDMS (semi-quantitative). An upper limit for a possible natural uranium contamination of 2.5 $pg\cdot\mu L^{-1}$ was observed. At this level the impact on the certified values is negligible. A turret of the gravimetrically prepared reference materials IRMM-075/3/4/5 with certified $n(^{236}U)/n(^{238}U)$ ratios extending to the order of 10^{-8} was also measured by MTE in order to calculate the background correction for MTE measurements at m/z = 236. This background is not coming from the presence of ^{236}U but rather from molecular interferences from the filament [5, 6]. A background count rate of 0.21 cps (counts per second) on the SEM was obtained for typical measurement conditions (see determination plot in annex 7). The isotopic composition of the used IRMM-3636a double spike solution was verified before and after the measurements to control the absence of contamination by the samples.

Materials, method reference materials used as calibrants and QC samples and sample mass are summarised in the table below (Table 4), Certificates of reference materials used in the characterisation are given in Annexes 2, 3, 4, 8 and 9.

Table 4: Summary of the methods and the CRMs used for each material to be characterised.

Materials	Methods	CRM/ double spike	QC samples	Uranium Sample mass (µg)
IRMM-019	Reverse-MTE	IRMM-074/10	IRMM-183, IRMM-075/1	6
IRMM-020	Reverse-MTE	IRMM-074/10	IRMM-183 IRMM-075/1	6
IRMM-021	MTE (minor isotope amount ratios) DS (major isotope amount ratio)	IRMM-074/10 IRMM-3636a	IRMM-075/4 IRMM-075/5 IRMM-074/10	4 4
IRMM-022	MTE (minor isotope amount ratios) DS (major isotope amount ratio)	IRMM-074/10 IRMM-3636a	IRMM-075/3 IRMM-075/4 IRMM-074/10	4 4
IRMM-023	Data from homogeneity study were used			
IRMM-024	MTE	IRMM-074/10	IRMM-187	4
IRMM-025	MTE	IRMM-074/10	IRMM-187	4
IRMM-026	MTE	IRMM-074/10	IRMM-187	4
IRMM-027	MTE	IRMM-074/10	IRMM-187	4
IRMM-028	MTE	IRMM-074/10	IRMM-187	4
IRMM-029	MTE	IRMM-074/10	IRMM-187	4

6.2 Evaluation of results

6.2.1 Technical evaluation

The obtained data were first checked for their validity based on technical reasons. In TIMS measurements, technical reasons to reject a replicate can be for example:

- An insufficient ion beam signal was collected

- The filament broke before the end of the measurement

- The method performance was not satisfactory, i.e. disagreement of the measurement results with the assigned value of the QC sample, or results which do not meet method performance criteria.

Based on the above criteria, some replicates were rejected as not technically valid and some complementary measurements were required for IRMM-019 and IRMM-021 (rejection of complete turrets due to insufficient method performance).

6.2.2 Data evaluation

The data evaluation depends on the method used to characterise the materials, due to the different corrections to be applied.

MTE and Reverse-MTE method:

The corrections applied for MTE and the discussion about uncertainty budgets are described in detail in [5, 6] and are described only briefly here. The mean major isotope amount ratio $n(^{235}U)/n(^{238}U)$) is externally corrected for mass fractionation by calculating the K-factor using the gravimetrically prepared reference material IRMM-074/10 measured on the same sample turret. This K-factor is influenced by analytical conditions and can vary slightly from one turret to the other.

For the minor isotope amount ratios, the calculation depends on the detectors used and the isotope amount ratios measured:

Case 1: if the minor isotopes are measured using Faraday cups (connected to amplifiers equipped with 10^{12} Ω resistors), the minor isotope amount ratios need to be corrected only for mass fractionation and peak tailing effects (i.e. contribution of the major isotopes to the minor isotopes).

Case 2: if the ratio $n(^{236}U)/n(^{238}U)$ is measured using the SEM ion counter, the measured ratios are corrected for the mass fractionation effect and for tailing effects as in case 1, but also for the background at mass m/z = 236. Furthermore an intercalibration factor between the Faraday cups and the SEM is applied, which is determined by measuring the ^{234}U on both the reference Faraday cup and the SEM during each measurement cycle [5, 6].

Case 3: if the ratio $n(^{234}U)/n(^{238}U)$ is measured on the SEM (Reverse-MTE), data are corrected for mass fractionation and tailing effects. In this case the intercalibration between the Faraday cups and the SEM ion counter is determined by measuring ^{234}U signal on both Faraday cup and SEM during each measurement cycle of the measurement.

Double spike measurements:

The major isotope amount ratio is internally corrected for the mass fractionation effect by calculating the K-factor on the isotope amount ratio $n(^{233}U)/n(^{236}U)$ from the double spike IRMM-3636a and applying it to the isotope amount ratio $n(^{235}U)/n(^{238}U)$ from the sample. The mean is calculated from the corrected data.

As two solutions (coming from conversions from two different daughter ampoules) are measured, the average major isotope amount ratio is calculated and the minor isotope amount ratios are subsequently normalised to this average value. For IRMM-021 to IRMM-023, the minor isotope ratios were measured by MTE, but then normalised to the mean major isotope amount ratio coming from separate measurements using the double spike method.

The contribution of the sources of uncertainties strongly depends on the magnitude of the isotope amount ratio and the method used to characterise the materials.

For the major isotope amount ratios measured by the DS method, the main uncertainty contribution in the budget is the uncertainty of the certified isotope amount ratio $n(^{233}U)/n(^{236}U)$ of the double spike reference material which represents more than 96 % of the relative combined uncertainty, leading to a $u_{char, rel}$ of about 0.008 %.

When the major isotope amount ratio is measured by MTE, the relative combined uncertainty comes from the MTE measurement of the sample, the MTE measurement of the reference material IRMM-074/10 used for the external mass fractionation correction and, with a slightly smaller proportion, also from the certified major isotope amount ratio of IRMM-074/10. Relative standard uncertainties for the characterisation are about 0.015 %.

Concerning the minor isotope amount ratios, the uncertainty budgets are more complicated due to the large dynamic range of the isotope amount ratios and to the different types of detectors used.

When ^{234}U is measured on the SEM (Reverse-MTE), the main source of uncertainty is clearly identified as being the contribution from the SEM calibration versus the Faraday cups and SEM linearity [6]. This represents more than 90 % of the relative combined uncertainty. The other sources (mass fractionation, counting statistics, etc.) represent only a few percent. The $u_{char,\ rel}$ is slightly above the SEM calibration uncertainty of 0.20 %. The same is observed when ^{236}U is measured on the SEM and ^{234}U is used for the intercalibration.

But with decreasing count rate, the counting statistics becomes increasingly dominant in the uncertainty budget. This means that the SEM calibration contribution becomes less dominant, it varies between 60 % and 75 % for IRMM-022 and IRMM-023, whereas the other contributions vary between 2 and 20 %. The background correction contribution is below 10 % for these two materials. The relative standard uncertainties for the characterisation are about 0.25 % for the isotope amount ratio $n(^{236}\text{U})/n(^{238}\text{U})$ in these materials.

In the special case of IRMM-021 with a $n(^{236}\text{U})/n(^{238}\text{U})$ ratio in the 10^{-8} range, the background correction at m/z = 236 becomes the main uncertainty source (more than 50 % of the total budget). The contribution of the SEM calibration is therefore only about 20 % and the other contributions are about 10 % - 15 % for IRMM-021. This leads to a relative standard uncertainty for the characterisation of 0.43 % for the isotope amount ratio $n(^{236}\text{U})/n(^{238}\text{U})$ of this material.

When the minor isotopes are measured on Faraday cups, the main uncertainty contributions change according to the range of the isotope amount ratios:

- If the isotope amount ratios are below 10^{-4}, the main contribution comes from the amplifier noise [17] encountered during the measurements themselves, whereas the (corrected) major isotope amount ratio used for mass fractionation correction of the minor isotope amount ratios represents only a few percent of the uncertainty budget. This leads to a relative standard uncertainty for the characterisation varying between 0.04 and 0.065 % for the concerned materials.

- If the minor isotope amount ratios are above 3×10^{-4}, the contribution of the major isotope amount ratio used for mass fractionation correction is the main source of uncertainty. The relative standard characterisation uncertainties vary between 0.01 % and 0.025 % for these isotope amount ratios.

- For minor isotope amount ratios between these two ranges a varying contribution of 20 % and 60 % to the uncertainty budget comes from the measurements (amplifier noise) and the normalisation. The relative standard characterisation uncertainties vary between 0.025 and 0.04 % for these isotope amount ratios.

6.3 Confirmation measurements

Confirmation measurements were performed using Gas Source Mass Spectrometry (GSMS). All the mother ampoules for each reference material and one of the daughter ampoules were measured. The agreement of the isotope amount ratios between the daughter ampoules was already confirmed within the characterisation exercise. GSMS measurements require one or two reference materials for correction of the measured isotope amount ratios, usually applied by sample-standard-bracketing. The former EC-171 series of UF_6 reference materials (equivalent to the solutions labelled IRMM-183 – IRMM-187 (see Annex 1)) was initially selected to serve as reference materials for the confirmation measurements. Nevertheless, the stock of the fluorinated EC-171 series is almost exhausted and only the data for one ampoule of the new IRMM-019 to IRMM-029 series could be confirmed independently (IRMM-029, ampoule 1). After this confirmation, the requirements for the certification of IRMM-029 ampoule 1 were fulfilled, because all the CRM characteristics had been successfully specified through the characterisation, homogeneity and stability studies. It was concluded that this material could be considered as being a reference material with assigned values and further used for GSMS measurements of the other materials. In a similar manner, each time when ampoules of another candidate reference material were confirmed, it was concluded that they could be used as reference material for confirmation measurements of the remaining materials.

In GSMS, for each measurement of a sample performed using two reference materials, several correction methods are available to evaluate the result: the 'memory corrected double standard' (MCDS) method or the single standard method using one or the other of the bracketing reference materials [13], which also includes memory correction. For the $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{238}U)$ isotope amount ratios all correction methods were found to be in agreement. However, due to the large dynamic range for the $n(^{236}U)/n(^{238}U)$ ratio the most applicable method has to be selected by the operator depending on the isotopic "distance" between the CRM and the sample, as described in [13]. Table 5 gives the number of ampoules to be analysed and the reference materials used (Annexes 8-11). For each material, the results of the confirmation measurements are plotted in Annex 12. Expanded uncertainties represented on these plots are strongly dominated by the uncertainties coming from the values of the material standards used as explained in [13]. For some individual runs the uncertainties are higher than for the other runs due to technical reason (outlier cycle during the run, loss of sensitivity).

The measurements of all ampoules confirmed the certification measurements, except one ampoule of IRMM-019, which is labelled and excluded from further distillation and distribution. This ampoule is not represented in Annex 12.

Table 5: List of methods and CRMs used for confirmation measurements

Material	Number of ampoules	CRM used	Material	Number of ampoules	CRM used
IRMM-019	5	IRMM-020 IRMM-025	IRMM-025	3	EC-171/071 IRMM-027
IRMM-020	3	IRMM-021 IRMM-025	IRMM-026	3	EC-171/071 IRMM-029 (A1)
IRMM-021	3	IRMM-022 IRMM-025	IRMM-027	3	EC-171/295 IRMM-029 (A1)
IRMM-022	3	EC-171/071 IRMM-025	IRMM-028	3	EC-171/295 IRMM-029 (A1)
IRMM-023	5	EC-171/071 IRMM-027	IRMM-029 ampoule 1 (A1)	1	EC-171/295 IRMM-171/446
IRMM-024	4	EC-171/295 IRMM-029 (A1)	IRMM-029 ampoule 2 (A2)	1	EC-171/295 IRMM-029 (A1)

Figure 8 shows the deviation between the average values of the major isotope amount ratio obtained by GSMS and the assigned values as defined in Section 7. The expanded uncertainties (k=2) represented in this plot are calculated using the uncertainties coming from averages of the confirmation measurements and the uncertainties from the assigned values. The uncertainties for the averages of the confirmation measurements are about the same as for the individual runs due to the uncertainties of the commonly used material standards for each of the candidate reference materials (see Annex 12 and Figure 8). This plot clearly shows the agreement between the assigned values and results for the confirmation measurements by GSMS for the major isotope amount ratios, which can therefore be certified.

Slightly larger uncertainties for the GSMS measurements were observed for IRMM-019, IRMM-020, IRMM-021 and IRMM-022 because these materials were confirmed using the single standard method. For IRMM-024, the larger uncertainty is due to an individual value measured with a larger uncertainty.

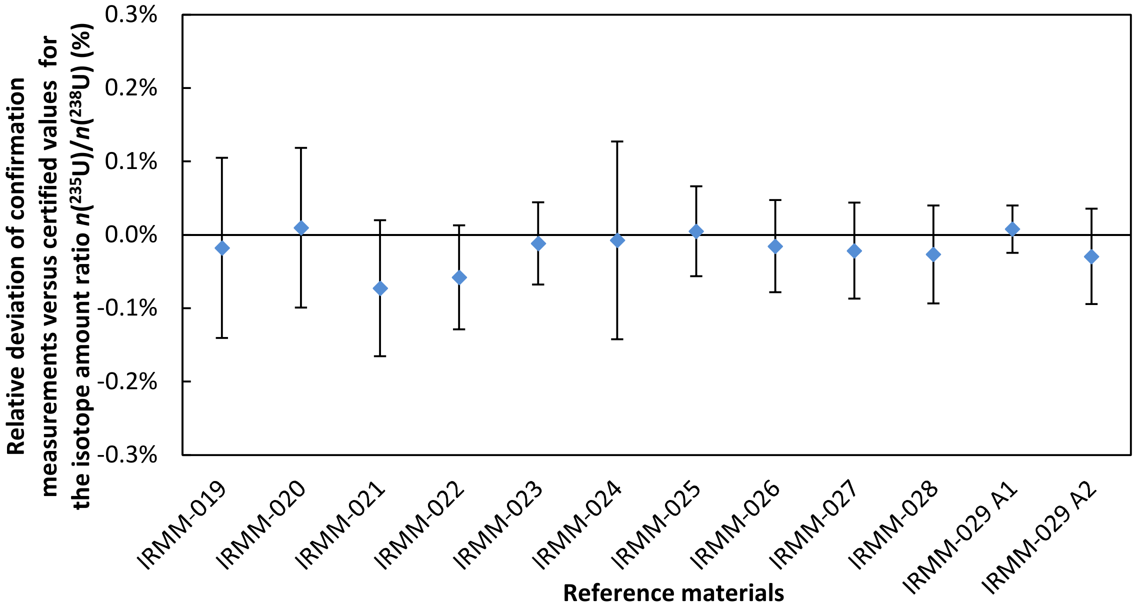

Figure 8: Relative deviation of the confirmation measurements versus the assigned values for the isotope amount ratio $n(^{235}U)/n(^{238}U)$ for each material. Expanded (k=2) uncertainties are represented, taking into account the uncertainties coming from the assigned values and uncertainties coming from the confirmation measurements.

Similarly, for the minor isotope amount ratios the deviations between the confirmation measurement results and the assigned values are represented in Figure 9 (for $n(^{234}U)/n(^{238}U)$) and Figure 10 (for $n(^{236}U)/n(^{238}U)$). The Figure 9 shows also that the confirmation measurement results validate the certification measurements within the uncertainties. The two materials measured using the single standard method have also a larger uncertainty as described before.

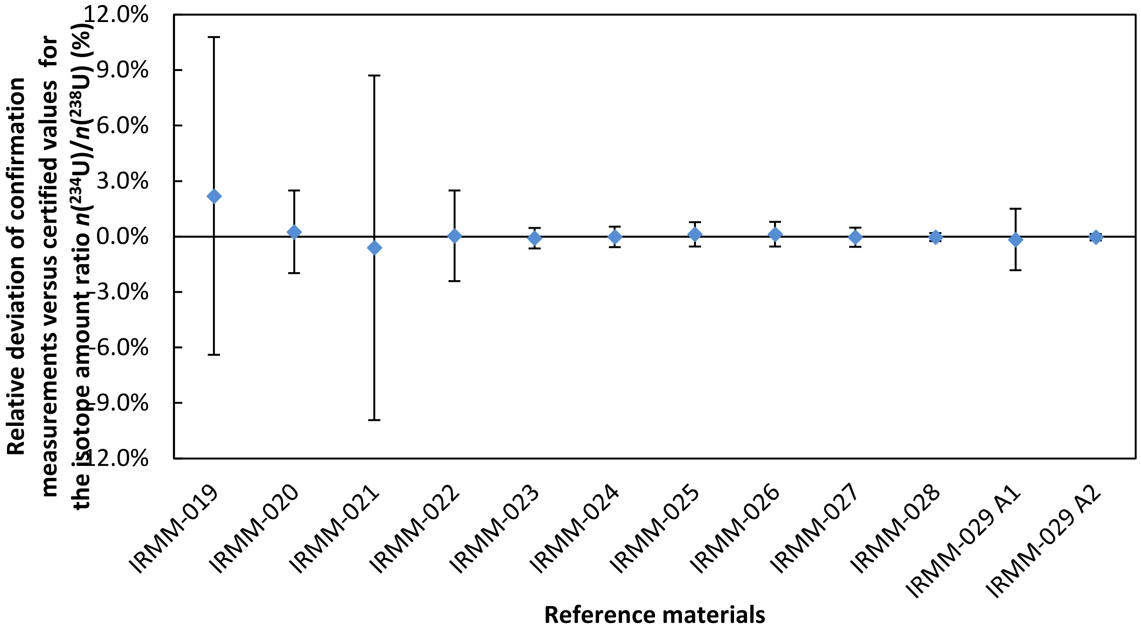

Figure 9: Relative deviation of the confirmation measurements versus the assigned values for the isotope amount ratio $n(^{234}U)/n(^{238}U)$ for each material. Expanded (k=2) uncertainties are represented, taking into account the uncertainties coming from the assigend values and uncertainties coming from the confirmation measurements.

On Figure 10, three materials (IRMM-021, IRMM-022 and IRMM-023) are not represented because the GSMS measurements gave results below the instrumental detection limit for the isotope amount ratio $n(^{236}U)/n(^{238}U)$. Here again the confirmation measurements are in agreement with the assigned values within uncertainties. Uncertainties are larger for IRMM-019 and IRMM-29 A1 (ampoule 1), due to the fact that the isotope amount ratios of the material standards are far away from the isotope amount ratios of these candidate materials.

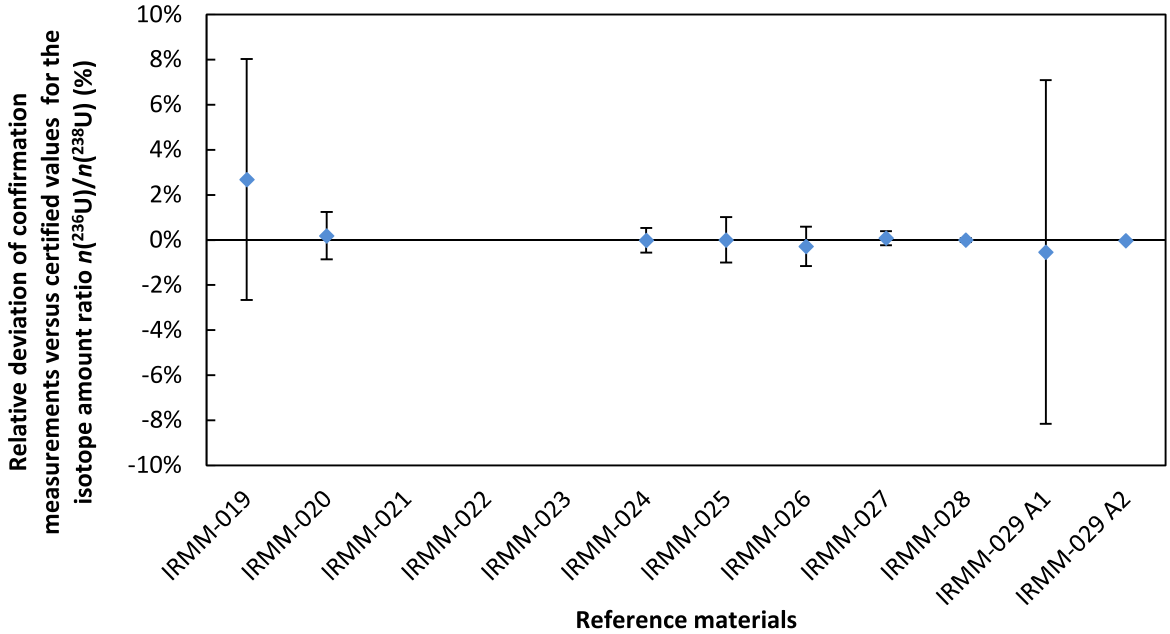

Figure 10: Relative deviation of the confirmation measurements versus the candidate values for the isotope amount ratio $n(^{236}U)/n(^{238}U)$ for each material. Expanded uncertainties (k=2) are represented, taking into account the uncertainties coming from

the assigned values and uncertainties coming from the confirmation measurements. The values for IRMM-021 to IRMM-023 are not represented because they are below the detection limit.

7 Value Assignment

Certified values were assigned based on the results of the characterisation measurements performed for materials of the IRMM-019 to IRMM-029 series. Certified values are values that fulfil the highest standards of accuracy. The certified values require metrological traceability associated with uncertainties [21]. Full uncertainty budgets in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [3] were established.

The assigned uncertainties for the isotope amount ratios consist of uncertainties related to characterisation, u_{char} (Section 6), potential between-unit inhomogeneity, u_{bb} (Section 4.1) and potential degradation during transport (u_{sts}) and long-term storage, u_{lts} (Section 5). The uncertainties related to degradation during transport and to long-term storage were found to be negligible. Therefore u_{char} and u_{bb} were combined to estimate the expanded, relative uncertainty of the certified value ($U_{CRM,\ rel}$) with a coverage factor k as:

$$U_{CRM,rel} = k \cdot \sqrt{u^2_{char,rel} + u^2_{bb,rel}} \qquad \textbf{Equation 7}$$

- u_{char} was estimated as described in Section 6
- u_{bb} was estimated as described in Section 4.1.

Because of the sufficient numbers of the degrees of freedom of the different uncertainty contributions, a coverage factor k of 2 was applied, to obtain the expanded uncertainties. The certified values and their uncertainties are summarised in Table 6.

Table 6: Certified values for isotope amount ratios and their uncertainties

Material/ isotope amount ratio	Certified value[1)] [mol/mol]	$u_{char,\ rel}$ [%]	$u_{bb,\ rel}$ [%]	$U_{CRM,\ rel}$[2)] [%]	U_{CRM}[3)] [mol/mol]
IRMM-019					
$n(^{234}U)/n(^{238}U)$	0.00000685	0.21	0.087	0.58	0.00000004
$n(^{235}U)/n(^{238}U)$	0.0016775	0.014	0.0038	0.030	0.0000005
$n(^{236}U)/n(^{238}U)$	0.00003652	0.064	0.098	0.25	0.00000009
IRMM-020					
$n(^{234}U)/n(^{238}U)$	0.00001192	0.20	0.066	0.50	0.00000006
$n(^{235}U)/n(^{238}U)$	0.0020957	0.014	0.0038	0.029	0.0000006
$n(^{236}U)/n(^{238}U)$	0.00028615	0.015	0.012	0.038	0.00000011
IRMM-021					
$n(^{234}U)/n(^{238}U)$	0.00002485	0.055	0.143	0.32	0.00000008
$n(^{235}U)/n(^{238}U)$	0.0044052	0.0080	0.0013	0.018	0.0000008
$n(^{236}U)/n(^{238}U)$	0.0000000266	0.43	1.39	3.01	0.0000000008
IRMM-022					
$n(^{234}U)/n(^{238}U)$	0.00005328	0.043	0.067	0.17	0.00000009
$n(^{235}U)/n(^{238}U)$	0.0072562	0.0080	0.0013	0.017	0.0000012
$n(^{236}U)/n(^{238}U)$	0.0000002415	0.24	0.46	1.08	0.0000000026

IRMM-023					
$n(^{234}U)/n(^{238}U)$	0.00033950	0.012	0.010	0.032	0.00000011
$n(^{235}U)/n(^{238}U)$	0.033881	0.0079	0.0013	0.018	0.000006
$n(^{236}U)/n(^{238}U)$	0.0000001153	0.25	0.67	1.47	0.0000000017
IRMM-024					
$n(^{234}U)/n(^{238}U)$	0.00029075	0.020	0.012	0.048	0.00000014
$n(^{235}U)/n(^{238}U)$	0.053254	0.014	0.0038	0.030	0.000016
$n(^{236}U)/n(^{238}U)$	0.00051696	0.010	0.0069	0.025	0.00000013
IRMM-025					
$n(^{234}U)/n(^{238}U)$	0.00012245	0.022	0.029	0.073	0.00000009
$n(^{235}U)/n(^{238}U)$	0.020436	0.013	0.0038	0.029	0.000006
$n(^{236}U)/n(^{238}U)$	0.00014839	0.014	0.024	0.061	0.00000009
IRMM-026					
$n(^{234}U)/n(^{238}U)$	0.00014941	0.024	0.0024	0.067	0.00000010
$n(^{235}U)/n(^{238}U)$	0.025679	0.014	0.0038	0.031	0.000008
$n(^{236}U)/n(^{238}U)$	0.00020730	0.020	0.017	0.053	0.00000011
IRMM-027					
$n(^{234}U)/n(^{238}U)$	0.00023159	0.023	0.015	0.056	0.00000013
$n(^{235}U)/n(^{238}U)$	0.041717	0.014	0.0038	0.031	0.000013
$n(^{236}U)/n(^{238}U)$	0.00038739	0.011	0.0092	0.031	0.00000012
IRMM-028					
$n(^{234}U)/n(^{238}U)$	0.00061041	0.021	0.0058	0.044	0.00000027
$n(^{235}U)/n(^{238}U)$	0.037576	0.015	0.0038	0.032	0.000012
$n(^{236}U)/n(^{238}U)$	0.0051943	0.011	0.00069	0.023	0.0000012
IRMM-029					
$n(^{234}U)/n(^{238}U)$	0.0008444	0.021	0.0042	0.047	0.0000004
$n(^{235}U)/n(^{238}U)$	0.044052	0.014	0.0038	0.032	0.000014
$n(^{236}U)/n(^{238}U)$	0.0105563	0.011	0.00034	0.022	0.0000023

1) The certified values are traceable to the International System of units (SI) via IRMM-074/10 or IRMM-3636a.

2) $u_{CRM,\,rel}$ are calculated from the rounded values of U_{CRM}.

3) Expanded (k = 2) and rounded uncertainty.

The isotope amount fractions are calculated as follows using the exact (and not the rounded) isotope amount ratios:

$$\frac{n(^{i}\mathrm{U})}{n(\mathrm{U})} = \frac{\frac{n(^{i}\mathrm{U})}{n(^{238}\mathrm{U})}}{\frac{n(^{234}\mathrm{U})}{n(^{238}\mathrm{U})}+\frac{n(^{235}\mathrm{U})}{n(^{238}\mathrm{U})}+\frac{n(^{236}\mathrm{U})}{n(^{238}\mathrm{U})}+\frac{n(^{238}\mathrm{U})}{n(^{238}\mathrm{U})}} \qquad \textbf{Equation 8}$$

where $n(^{i}U)/n(U)$ is the isotope amount fraction of the isotope ^{i}U and $n(^{238}U)/n(^{238}U)$ is equal to 1. Uncertainties were calculated with the exact (and not the rounded) standard uncertainties of the isotope amount ratios in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [3]. Due to a sufficient degree of freedom a coverage factor k of 2 was applied. The certified values and their uncertainties are summarised in Table 7.

Table 7 : Certified isotope amount fractions and their uncertainties

Material/ isotope amount fraction	Certified value[1)] [mol/mol]	U_{CRM}[2)] [mol/mol]	Material/ isotope amount fraction	Certified value[1)] [mol/mol]	U_{CRM}[2)] [mol/mol]
IRMM-019			IRMM-025		
$n(^{234}\text{U})/n(\text{U}) \times 100$	0.000683	0.000004	$n(^{234}\text{U})/n(\text{U}) \times 100$	0.011997	0.000009
$n(^{235}\text{U})/n(\text{U}) \times 100$	0.16746	0.00005	$n(^{235}\text{U})/n(\text{U}) \times 100$	2.0021	0.0006
$n(^{236}\text{U})/n(\text{U}) \times 100$	0.003646	0.000009	$n(^{236}\text{U})/n(\text{U}) \times 100$	0.014538	0.000009
$n(^{238}\text{U})/n(\text{U}) \times 100$	99.82821	0.00005	$n(^{238}\text{U})/n(\text{U}) \times 100$	97.9714	0.0006
IRMM-020			IRMM-026		
$n(^{234}\text{U})/n(\text{U}) \times 100$	0.001189	0.000005	$n(^{234}\text{U})/n(\text{U}) \times 100$	0.014562	0.000010
$n(^{235}\text{U})/n(\text{U}) \times 100$	0.20907	0.00006	$n(^{235}\text{U})/n(\text{U}) \times 100$	2.5027	0.0008
$n(^{236}\text{U})/n(\text{U}) \times 100$	0.028547	0.000011	$n(^{236}\text{U})/n(\text{U}) \times 100$	0.020204	0.000011
$n(^{238}\text{U})/n(\text{U}) \times 100$	99.76119	0.00007	$n(^{238}\text{U})/n(\text{U}) \times 100$	97.4625	0.0008
IRMM-021			IRMM-027		
$n(^{234}\text{U})/n(\text{U}) \times 100$	0.002474	0.000008	$n(^{234}\text{U})/n(\text{U}) \times 100$	0.022218	0.000013
$n(^{235}\text{U})/n(\text{U}) \times 100$	0.43858	0.00008	$n(^{235}\text{U})/n(\text{U}) \times 100$	4.0023	0.0012
$n(^{236}\text{U})/n(\text{U}) \times 100$	0.00000265	0.00000008	$n(^{236}\text{U})/n(\text{U}) \times 100$	0.037166	0.000011
$n(^{238}\text{U})/n(\text{U}) \times 100$	99.55895	0.00008	$n(^{238}\text{U})/n(\text{U}) \times 100$	95.9383	0.0012
IRMM-022			IRMM-028		
$n(^{234}\text{U})/n(\text{U}) \times 100$	0.005289	0.000009	$n(^{234}\text{U})/n(\text{U}) \times 100$	0.058503	0.000026
$n(^{235}\text{U})/n(\text{U}) \times 100$	0.72035	0.00012	$n(^{235}\text{U})/n(\text{U}) \times 100$	3.6014	0.0011
$n(^{236}\text{U})/n(\text{U}) \times 100$	0.00002397	0.00000025	$n(^{236}\text{U})/n(\text{U}) \times 100$	0.49783	0.00011
$n(^{238}\text{U})/n(\text{U}) \times 100$	99.27433	0.00012	$n(^{238}\text{U})/n(\text{U}) \times 100$	95.8423	0.0011
IRMM-023			IRMM-029		
$n(^{234}\text{U})/n(\text{U}) \times 100$	0.032827	0.000011	$n(^{234}\text{U})/n(\text{U}) \times 100$	0.08001	0.00004
$n(^{235}\text{U})/n(\text{U}) \times 100$	3.2760	0.0006	$n(^{235}\text{U})/n(\text{U}) \times 100$	4.1737	0.0012
$n(^{236}\text{U})/n(\text{U}) \times 100$	0.00001115	0.00000016	$n(^{236}\text{U})/n(\text{U}) \times 100$	1.00017	0.00021
$n(^{238}\text{U})/n(\text{U}) \times 100$	96.6911	0.0006	$n(^{238}\text{U})/n(\text{U}) \times 100$	94.7461	0.0012
IRMM-024					
$n(^{234}\text{U})/n(\text{U}) \times 100$	0.027584	0.000013			
$n(^{235}\text{U})/n(\text{U}) \times 100$	5.0523	0.0014			
$n(^{236}\text{U})/n(\text{U}) \times 100$	0.049045	0.000013			
$n(^{238}\text{U})/n(\text{U}) \times 100$	94.8711	0.0014			

1) These values are calculated using the isotope amount ratios and therefore traceable to the SI.

2) Expanded (k = 2) and rounded uncertainty.

The molar masses of uranium were also calculated as follows for each uranium hexafluoride reference material using the isotope molar mass given in [22] and using the exact (and not rounded) isotope amount fraction calculated above:

$$\mathbf{M}(\mathbf{U}) = \frac{n(^{234}\mathbf{U})}{n(\mathbf{U})} \times \mathbf{M}(^{234}\mathbf{U}) + \frac{n(^{235}\mathbf{U})}{n(\mathbf{U})} \times \mathbf{M}(^{235}\mathbf{U}) + \frac{n(^{236}\mathbf{U})}{n(\mathbf{U})} \times \mathbf{M}(^{236}\mathbf{U}) + \frac{n(^{238}\mathbf{U})}{n(\mathbf{U})} \times \mathbf{M}(^{238}\mathbf{U})$$

Equation 9

M(U) is the molar mass of uranium in the certified reference materials, M(^{i}U) is the molar mass of the isotope ^{i}U given in [22], $n(^{i}U)/n(U)$ is the isotope amount fraction of the isotope ^{i}U calculated above. Uncertainties were calculated with the exact (and not rounded) standard uncertainty of the isotope amount fraction and the uncertainties given in [22] for isotope molar masses in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [3]. Due to a sufficient degree of freedom a coverage factor *k* of 2 was applied. The certified values and their uncertainties are summarised in Table 8.

Table 8: Certified uranium molar masses and their uncertainties

Material/ uranium molar mass	Certified value[1)] [g·mol^{-1}]	U_{CRM}[2)] [g·mol^{-1}]	Material/ uranium molar mass	Certified value[1)] [g·mol^{-1}]	U_{CRM}[2)] [g·mol^{-1}]
IRMM-019 M(U)	238.045652	0.000005	IRMM-025 M(U)	237.989815	0.000017
IRMM-020 M(U)	238.043882	0.000005	IRMM-026 M(U)	237.974545	0.000022
IRMM-021 M(U)	238.037502	0.000005	IRMM-027 M(U)	237.92881	0.00004
IRMM-022 M(U)	238.028916	0.000006	IRMM-028 M(U)	237.93017	0.00004
IRMM-023 M(U)	237.950966	0.000016	IRMM-029 M(U)	237.90203	0.00004
IRMM-024 M(U)	237.89678	0.00005			

1) These values are calculated using the isotope amount ratios and therefore traceable to the SI.

2) Expanded (*k* = 2) and rounded uncertainty.

Finally the isotope mass fractions were calculated for each certified reference materials using the previous exact and not rounded values and the isotope molar mass given in [22] as following:

$$\frac{m(\,^{i}\mathrm{U})}{m(\mathrm{U})} = \frac{n(\,^{i}\mathrm{U})}{n(\mathrm{U})} \times \frac{\mathrm{M}(\,^{i}\mathrm{U})}{\mathrm{M}(\mathrm{U})}$$ **Equation 10**

$m(^{i}U)/m(U)$ the isotope mass fractions of the isotope ^{i}U. All the other parameters are defined above. Uncertainties were calculated with the exact (and not rounded) standard uncertainty of the isotope amount fraction and uranium molar masses. For the isotope molar masses the uncertainties given in [22] are used. All the uncertainties were established in accordance with the 'Guide to the Expression of Uncertainty in Measurement' [3]. Due to a sufficient degree of freedom a coverage factor *k* of 2 was applied. The certified values and their uncertainties are summarised in Table 9.

Table 9: Certified isotope mass amount and their uncertainties

Material/ isotope mass fraction	Certified value[1] [g/g]	U_{CRM}[2] [g/g]	Material/ isotope mass fraction	Certified value[1] [g/g]	U_{CRM}[2] [g/g]
IRMM-019			IRMM-025		
$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.000672	0.000004	$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.011798	0.000009
$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	0.16535	0.00005	$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	1.9773	0.0006
$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.003615	0.000009	$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.014419	0.000009
$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	99.83036	0.00005	$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	97.9965	0.0006
IRMM-020			IRMM-026		
$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.001169	0.000005	$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.014321	0.000010
$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	0.20644	0.00006	$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	2.4719	0.0007
$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.028307	0.000011	$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.020040	0.000011
$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	99.76409	0.00007	$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	97.4937	0.0007
IRMM-021			IRMM-027		
$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.002432	0.000008	$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.021855	0.000012
$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	0.43306	0.00007	$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	3.9538	0.0012
$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.00000262	0.00000008	$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.036871	0.000011
$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	99.56450	0.00007	$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	95.9875	0.0012
IRMM-022			IRMM-028		
$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.005200	0.000009	$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.057547	0.000026
$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	0.71132	0.00012	$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	3.5577	0.0011
$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.00002377	0.00000025	$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.49389	0.00011
$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	99.28346	0.00012	$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	95.8909	0.0011
IRMM-023			IRMM-029		
$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.032288	0.000011	$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.07871	0.00004
$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	3.2360	0.0005	$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	4.1236	0.0012
$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.00001106	0.00000016	$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.99237	0.00021
$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	96.7317	0.0005	$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	94.8054	0.0012
IRMM-024					
$m^{234}\mathrm{U})/m(\mathrm{U})$ ×100	0.027137	0.000013			
$m(^{235}\mathrm{U})/m(\mathrm{U})$ ×100	4.9917	0.0014			
$m(^{236}\mathrm{U})/m(\mathrm{U})$ ×100	0.048663	0.000013			
$m(^{238}\mathrm{U})/m(\mathrm{U})$ ×100	94.9325	0.0014			

1) These values are calculated using the isotope amount ratios and therefore traceable to the SI.

2) Expanded (k = 2) and rounded uncertainty.

8 Metrological traceability and commutability

8.1 Metrological traceability

The certified values for IRMM-021, IRMM-022 and IRMM-023 are traceable to the International System of units (SI) via IRMM-3636a. All the other materials are traceable to the SI via IRMM-074/10.

It was shown in [10], that the isotope amount ratio $n(^{233}U)/n(^{236}U)$ of IRMM-3636a was confirmed by TIMS measurements using the major isotope amount ratio $n(^{235}U)/n(^{238}U)$ of IRMM-074/10 as calibrant, the same as used for all MTE measurements within this project. The relative difference between the $n(^{233}U)/n(^{236}U)$ result obtained for the confirmation measurement [10] and the certified value (from gravimetry) was 0.003 (±0.022) % (coverage factor k=2), which is insignificant. This was also confirmed (in a reverse manner) by measuring IRMM-074/10 as QC sample using the DS method versus IRMM-3636a within this project when applying the DS method.

In conclusion, the assigned values for all materials of the IRMM-019 to IRMM-029 series, including IRMM-021, IRMM-022 and IRMM-023 which were measured using the DS method, are traceable to the certified values of the same calibrant, IRMM-074/10.

8.2 Commutability

Many measurement procedures include one or more steps, which are selecting specific analytes or specific groups of analytes from the sample for the subsequent steps of the whole measurement process. Often the complete identity of these 'intermediate analytes' is not fully known or taken into account. Therefore, it is difficult to mimic all the analytically relevant properties of real samples within a CRM. The degree of equivalence in the analytical behaviour of real samples and a CRM with respect to various measurement procedures (methods) is summarised in a concept called 'commutability of a reference material'. There are various definitions expressing this concept. For instance, the CLSI Guideline C-53A [23] recommends the use of the following definition for the term *commutability*:

> "The equivalence of the mathematical relationships among the results of different measurement procedures for a RM and for representative samples of the type intended to be measured."

The commutability of a CRM defines its fitness for use and, thus, it is a crucial characteristic in case of the application of different measurement methods. When commutability of a CRM is not established, the results from routinely used methods cannot be legitimately compared with the certified value to determine whether a bias does not exist in calibration, nor can the CRM be used as a calibrant.

The IRMM-019 to IRMM-029 series is a set of uranium hexafluoride reference materials certified for uranium isotope amount ratios, isotope amount fraction, isotope mass fraction and uranium molar mass. These reference materials are tailor-made by IRMM and are intended to serve as calibrants for isotope mass spectrometry measurements.

9 Instructions for use

9.1 Safety information

The IRMM-019 to IRMM-029 series contains radioactive material. The ampoules should be handled with great care and by experienced personnel in a laboratory suitably equipped for the safe handling of radioactive materials.

9.2 Storage conditions

The materials shall be stored at room temperature.

Please note that the European Commission cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially of opened ampoules.

9.3 Preparation and use of the material

This series of reference materials is used to serve as a calibrants for isotope mass spectrometry measurements. Prior to use, it is recommended to cool the ampoule with a dry ice-ethanol mixture at about -70 °C and evacuate the ampoule under vacuum (pressure below 1×10^{-2} mbar). For safety reasons, the vacuum line should be connected to a cold trap.

9.4 Minimum sample intake

Based on physical reasons, there is no minimum sample intake to be taken into account.

9.5 Use of the certified value

The main purpose of these materials is to be used as calibrant in uranium hexafluoride GSMS. After conversion of the material (see section about processing), the material can be used as calibrant also for isotope mass spectrometry techniques such as TIMS and ICP-MS. As any reference material, they can also be used for assessing the method performance (checking accuracy of analytical results/calibration), for quality control purpose or validation studies.

Use as a calibrant

The uncertainty of the certified value shall be taken into account in the estimation of the measurement uncertainty.

Comparing an analytical result with the certified value

A result is unbiased if the combined standard uncertainty of measurement and certified value covers the difference between the certified value and the measurement result (see also ERM Application Note 1, www.erm-crm.org [24]).

For assessing the method performance, the measured values of the CRMs are compared with the certified values. The procedure is described here in brief:

- Calculate the absolute difference between mean measured value and the certified value (Δ_{meas}).
- Combine measurement uncertainty (u_{meas}) with the uncertainty of the certified value (u_{CRM}): $u_\Delta = \sqrt{u_{meas}^2 + u_{CRM}^2}$
- Calculate the expanded uncertainty (U_Δ) from the combined uncertainty ($u_{\Delta,}$) using an appropriate coverage factor, corresponding to a level of confidence of approximately 95 %
- If $\Delta_{meas} \leq U_\Delta$ no significant difference between the measurement result and the certified value, at a confidence level of about 95 % exists.

Use for quality control purpose

The certified values can be used for quality control charts. Different CRM-units will give the same result, because inhomogeneity was included in the uncertainties of the certified values.

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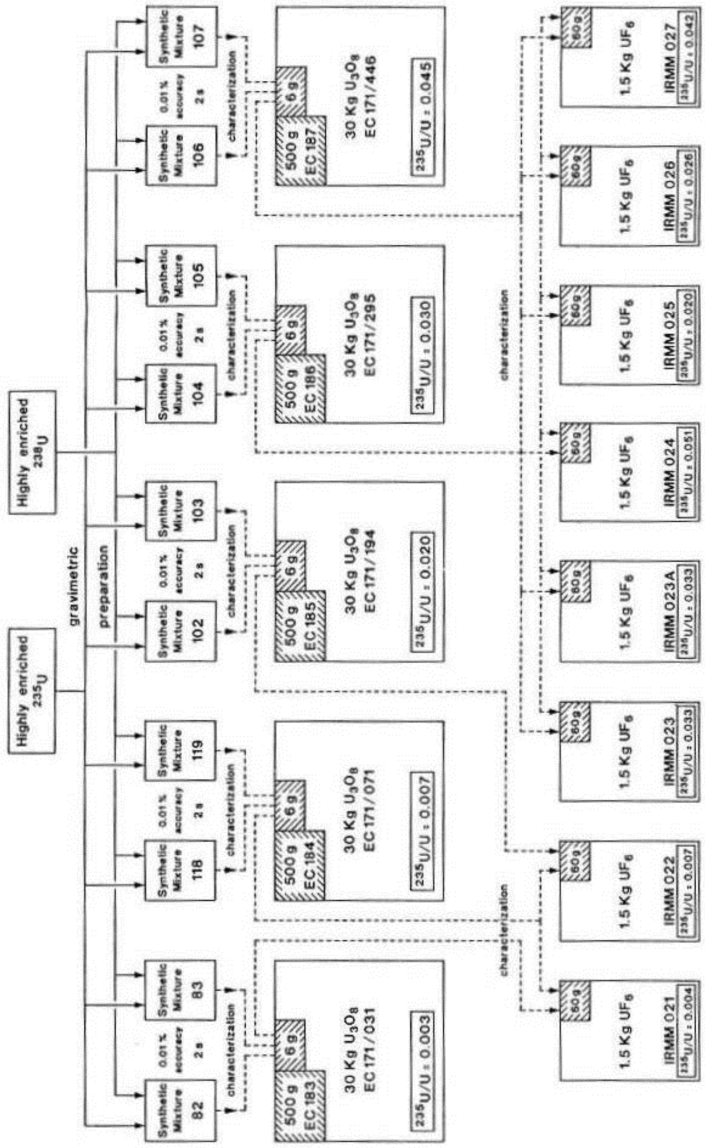
23 H. Vesper, H. Emons, M. Gnezda, C. P. Jain, W. G. Miller, R. Rej, G. Schumann, J. Tate, L. Thienpont, J. E. Vaks, Characterization and Qualification of Commutable Reference Materials for Laboratory Medicine; Approved Guideline, CLSI document C53-A, Clinical and Laboratory Standards Institute, Wayne, PA, USA, 2010

24 T.P.J. Linsinger, ERM Application Note 1: Comparison of a measurement result with the certified value, www.erm-crm.org (last accessed on 14/05/2014)

Annexes

Annex 1: Scheme for previous certification of UF_6 reference materials, including:

- Set of two "starting materials", highly enriched in ^{235}U and ^{238}U
- Set of 10 gravimetrically prepared mixtures, subsequently fluorinated
- IRMM-171 series (labelled EC171 here), 30 kg of oxides, 6 g were fluorinated and characterised by GSMS using the set of 10 mixtures
- IRMM-183 – IRMM-187 series, solutions (labelled EC183 – EC-187 here), prepared by dissolving 500g of IRMM-171 series
- IRMM-021- IRMM-027 (later extended towards IRMM-019 – IRMM-029), characterised by GSMS using fluorinated IRMM-171 series



Annex 2: Certificate of IRMM-074 series (IRMM-074/1-10)

IRMM

Institute for Reference Materials and Measurements

CERTIFICATE

ISOTOPIC REFERENCE MATERIAL IRMM-074

The Isotopic Reference Material IRMM-074 is a set of mixtures of uranium isotopes ^{233}U, ^{235}U and ^{238}U with molar ratios certified as follows:

Code Number	Molar Isotope Abundance Ratio		
	$n(^{233}U)/n(^{235}U)$ U = 0.025% (relative)	$n(^{233}U)/n(^{238}U)$ U = 0.025%(relative)	$n(^{235}U)/n(^{238}U)$ U = 0.015%(relative)
IRMM-074/1	1.026 85	1.027 11	1.000 254
IRMM-074/2	0.307 993	0.308 072	1.000 258
IRMM-074/3	0.010 228 8	0.010 231 4	1.000 259
IRMM-074/4	0.003 073 58	0.003 074 37	1.000 259
IRMM-074/5	0.001 030 61	0.001 030 88	1.000 259
IRMM-074/6	0.000 307 778	0.000 307 858	1.000 259
IRMM-074/7	0.000 102 603	0.000 102 629	1.000 259
IRMM-074/8	0.000 030 801 1	0.000 030 809 1	1.000 259
IRMM-074/9	0.000 008 158 7	0.000 008 160 8	1.000 259
IRMM-074/10	0.000 001 018 86	0.000 001 019 13	1.000 259

The Isotopic Reference Material is intended for the verification and correction of non-linearities of the entire mass spectrometer measurement system.

NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against these Isotopic Reference Materials will, therefore, also be traceable to the SI unit system.

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2. The uncertainties as specified in the table can be considered as expanded uncertainties U where $k = 2$. The value of the standard uncertainty can therefore be derived: $u_c = U \cdot 0.5$
The uncertainties given are supported by calculation of the combined uncertainty following the ISO/GUM recommendations[1] and are based on measured values of the isotopic enrichments, the weights of oxides and solutions, and of the impurity levels. The uncertainties were also confirmed through comparison measurements made on samples of IRMM-072, IRMM-199 and CRM-U-500 (DOE/NBL).
3. Values for molar isotope abundance ratios are valid for June 2005.
4. The Isotopic Reference Material IRMM-074 consists of a set of 10 units. Each unit consists of approximately 0.2 mg uranium as uranylnitrate in 2 mL 1 M nitric acid solution in a sealed quartz glass ampoule.
5. The atomic masses, used in the calculations, are[2]

^{233}U: 233.039 627 0(60) g·mol^{-1}
^{234}U: 234.040 944 7(44) g·mol^{-1}
^{235}U: 235.043 922 2(42) g·mol^{-1}
^{236}U: 236.045 561 0(42) g·mol^{-1}
^{238}U: 238.050 783 5(44) g·mol^{-1}

6. The vial should by opened with great care and by experienced personnel in a laboratory environment suitably equipped for the safehandling of radioactive materials.
7. Full details on the certification procedure can be found in the Certification Report EUR 22270 EN[3].

Chemical purification of the $^{233}U_3O_8$, $^{235}U_3O_8$ and $^{238}U_3O_8$ starting materials was performed by R Eykens.

Weighing and preparation of the Isotopic Reference Material was performed by F Hendrickx and R Eykens. Characterization of the enriched isotopes from which the set was prepared and verification measurements on the mixtures, were performed by S Richter on samples prepared by F Kehoe and A Alonso Muñoz. The ampoulation of this Isotopic Reference Material was accomplished by G Van Baelen and A Verbruggen.

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

B-2440 GEEL	P Taylor	R Wellum
July 2006	Head	IRMM Safeguards Coordinator
	Isotope Measurements Unit	

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993
[2] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[3] A. Verbruggen, A. Alonso, R. Eykens, F. Hendrickx, F. Kehoe, H. Kühn, S. Richter, G. Van Baelen, R.Wellum, Preparation and certification of IRMM-074, a new set of uranium isotope mixtures for calibration of mass spectrometers, Report EUR 22270 EN

Annex 3: Certificate of IRMM-3636a

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for reference materials and measurements
Isotope Measurements (Geel)

CERTIFICATE
SPIKE ISOTOPIC REFERENCE MATERIAL IRMM-3636a

2.119 06(26) · 10^{-7} mol (^{236}U) · g^{-1} (solution)

The Spike Isotopic Reference Material is supplied with an isotope amount content of ^{236}U certified as above.

The amounts of other uranium isotopes present are related to the ^{236}U content through the following certified amount ratios:

$n(^{233}U)/n(^{236}U)$:	1.019 06(16)
$n(^{234}U)/n(^{236}U)$:	0.000 366 06(48)
$n(^{235}U)/n(^{236}U)$:	0.000 045 480(74)
$n(^{238}U)/n(^{236}U)$:	0.000 234 81(38)

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	50.455 8(39)	$m(^{233}U)/m(U)$	50.135 5(39)
$n(^{234}U)/n(U)$	0.018 125(24)	$m(^{234}U)/m(U)$	0.018 087(24)
$n(^{235}U)/n(U)$	0.002 251 8(37)	$m(^{235}U)/m(U)$	0.002 256 8(37)
$n(^{236}U)/n(U)$	49.512 2(39)	$m(^{236}U)/m(U)$	49.832 4(39)
$n(^{238}U)/n(U)$	0.011 626(19)	$m(^{238}U)/m(U)$	0.011 801(19)

The molar mass of the uranium in this sample is 234.528 74(12) g·mol^{-1}

From the certified values, the following amount content and mass fractions are derived:

4.279 88(54) · 10^{-7}	mol (U) · g^{-1} (solution)
2.159 45(35) · 10^{-7}	mol (^{233}U) · g^{-1} (solution)
1.003 75(13) · 10^{-4}	g (U) · g^{-1} (solution)
0.500 195(62) · 10^{-4}	g (^{236}U) · g^{-1} (solution)
0.503 237(81) · 10^{-4}	g (^{233}U) · g^{-1} (solution)

Retieseweg 111, B-2440 Geel - Belgium. Telephone: (32-14) 571 211. http://irmm.jrc.ec.europa.eu 06/2009

NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against this Isotopic Reference Material will, therefore, also be traceable to the SI unit system.

2. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following ISO/GUM recommendations[1]. They are given in parentheses and include a coverage factor k=2. They apply to the last two digits of the value. The values certified are traceable to the SI.

3. This Reference Material was prepared by metrological dilution of IRMM-3636 which was prepared by metrological weighing of high enriched uranium base materials. and dissolution in HNO_3. Subsequently the diluted solution was dispensed into individual units.

4. Values for molar isotope abundance ratios are valid for 1 July 2007.

5. The Isotopic Reference Material IRMM-3636a comes in a flame-sealed quartz ampoule containing about 0.42 µmol uranium in about 1 mL of a chemically stable 1 M nitric acid solution.

6. The atomic masses, used in the calculations, are[2]

^{233}U : 233.039 627 0 (60) $g \cdot mol^{-1}$
^{234}U : 234.040 944 7 (44) $g \cdot mol^{-1}$
^{235}U : 235.043 922 2 (42) $g \cdot mol^{-1}$
^{236}U : 236.045 561 0 (42) $g \cdot mol^{-1}$
^{238}U : 238.050 783 5 (44) $g \cdot mol^{-1}$

7. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

8. Full details on the certification procedure can be found in the Certification Report EUR 23408 EN [3]

Chemical purification of the $^{236}U_3O_8$ and $^{233}U_3O_8$ starting materials was performed by R Eykens and F Kehoe.

Weighing and preparation of the Isotopic Reference Material was performed by R Eykens. The ampoulation of this Isotopic Reference Material was accomplished by S Werelds, M Peeters, R Eykens and A Verbruggen.

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993
[2] G. Audi and A.H. Wapstra, The 2003 atomic mass evaluation, Nucl Phys A729(2003) 337-676.
[3] A. Verbruggen, A. Alonso, R. Eykens, F. Kehoe, H. Kühn, S. Richter, Y. Aregbe, Preparation and certification of IRMM-3636 and 3636a, Report EUR 23408 EN

Characterization of the enriched isotopes from which IRMM-3636 was prepared and verification measurements were performed by S Richter and H Kühn on samples prepared by F Kehoe and A Alonso Muñoz.

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

B-2440 GEEL	P Taylor	Y Aregbe
May 2008 Revised June 2009	Head Isotope Measurements Unit	IRMM Safeguards Coordinator

Annex 4: Certificate IRMM-075

IRMM
Institute for Reference Materials and Measurements

CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-075

The Isotopic Reference Material IRMM-075 is a set of mixtures of uranium isotopes ^{236}U and ^{nat}U with molar ratios certified as follows:

Code Number	Molar Isotope Abundance Ratio
	$n(^{236}U)/n(^{238}U)$
IRMM-075/1	1.044 33(37) $\cdot 10^{-4}$
IRMM-075/2	1.141 60(40) $\cdot 10^{-5}$
IRMM-075/3	1.040 93(36) $\cdot 10^{-6}$
IRMM-075/4	1.137 42(40) $\cdot 10^{-7}$
IRMM-075/5	1.065 19(75) $\cdot 10^{-8}$
IRMM-075/6	1.088 5(63) $\cdot 10^{-9}$

The Isotopic Reference Material is intended for the verification and correction of non-linearities of the entire mass spectrometer measurement system.

NOTES

1. This Isotopic Reference Material is traceable to the international SI unit for amount of substance - the mole - via synthetic mixtures prepared at IRMM. Measurements calibrated against these Isotopic Reference Materials will, therefore, also be traceable to the SI unit system.
2. The uncertainties as specified in the table can be considered as expanded uncertainties U where $k = 2$. The value of the standard uncertainty can therefore be derived: $u_c = U \cdot 0.5$. The uncertainties given are supported by calculation of the combined uncertainty following the ISO/GUM recommendations[1] and are based on measured values of the isotopic enrichments, the weights of oxides and solutions, and of the impurity levels.

[1] International Organisation for Standardisation, Guide to the expression of Uncertainty in Measurement, ©ISO, ISBN 92-67-10188-9, Geneva, Switzerland, 1993

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3. Values for molar isotope abundance ratios are valid for 6 May 2006.
4. The Isotopic Reference Material IRMM-075 consists of a set of 6 units. Each unit consists of approximately 1 mg uranium as uranylnitrate in 1 mL 1 M nitric acid solution in a sealed quartz glass ampoule.
5. The atomic masses, used in the calculations, are[2]

^{233}U: 233.039 627 0(60) g·mol^{-1}
^{234}U: 234.040 944 7(44) g·mol^{-1}
^{235}U: 235.043 922 2(42) g·mol^{-1}
^{236}U: 236.045 561 0(42) g·mol^{-1}
^{238}U: 238.050 783 5(44) g·mol^{-1}

6. The vial should be opened with great care and by experienced personnel in a laboratory environment suitably equipped for the safehandling of radioactive materials.
7. Full details on the certification procedure can be found in the Certification Report[3].

Chemical purification of the $^{236}U_3O_8$ and $^{nat}U_3O_8$ starting materials was performed by R Eykens and F Kehoe.

Weighing and preparation of the Isotopic Reference Material was performed by R Eykens. The ampoulation of this Isotopic Reference Material was accomplished by S Werelds. E Joos. M Peeters, R Eykens and A Verbruggen.

Characterization of the enriched isotopes from which the set was prepared and verification measurements on the mixtures were performed by S Richter on samples prepared by F Kehoe and A Alonso Muñoz.

The overall coordination leading to the establishment, certification and issuance of this Isotopic Reference Material set and of the preparation and issuance of the certificate was performed by A Verbruggen.

B-2440 GEEL August 2007	Y Aregbe IRMM Safeguards Coordinator	P Taylor Head Isotope Measurements Unit

[2] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation Nucl Phys A565 (1993) 1-65

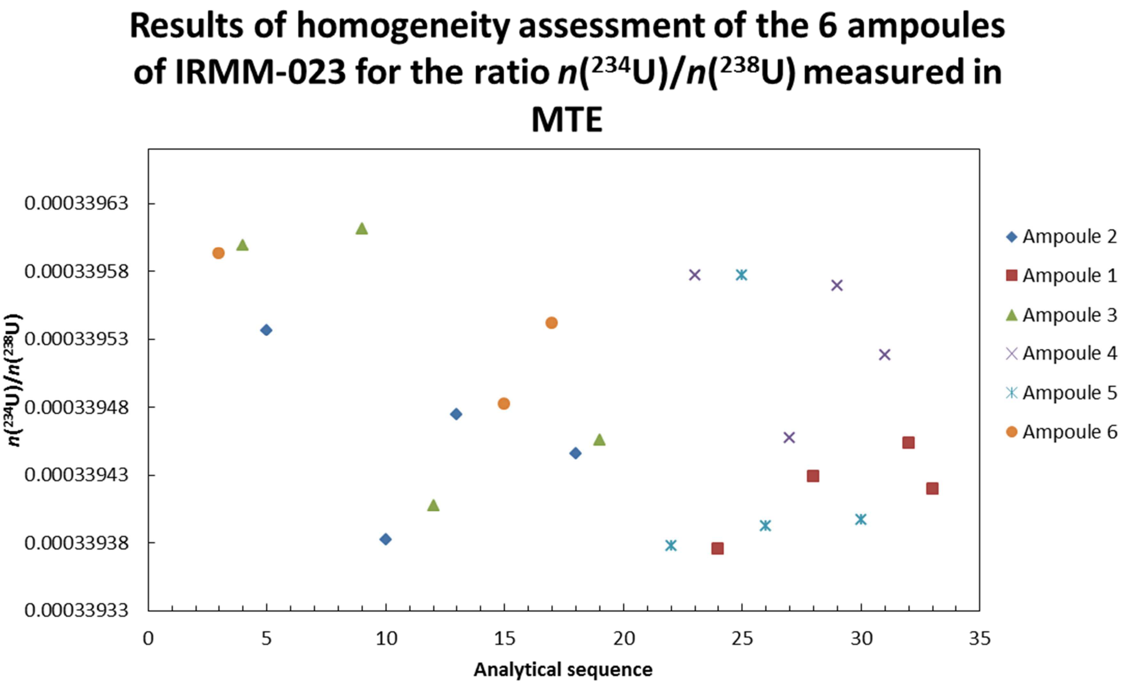
[3] A. Verbruggen, A. Alonso, R. Eykens, F. Kehoe, H. Kühn, S Richter R Wellum, Y. Aregbe, Preparation and certification of IRMM-075, Report EUR .... EN

Annex 5: Homogeneity study on IRMM-023

Annex 5.1: Results of homogeneity assessment of the 6 ampoules of IRMM-023 for the ratio $n(^{234}U)/n(^{238}U)$ measured in MTE. Technical outliers are not represented.

Measurements from 1 to 21 were performed on magazine 1.

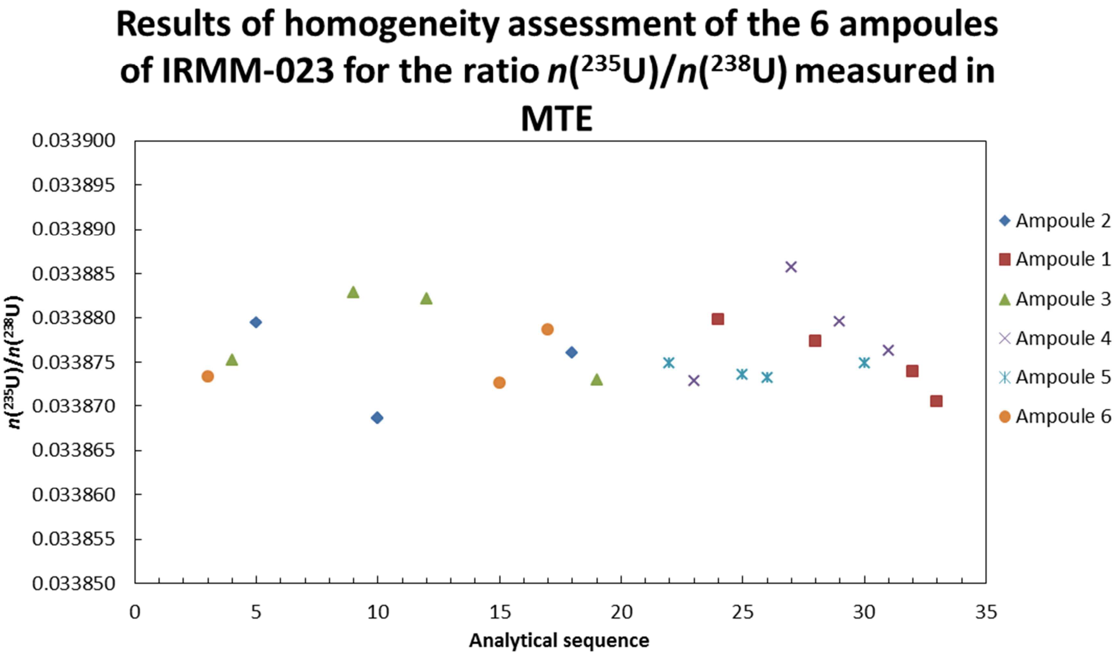
Measurements from 22 to 33 were performed on magazine 2.



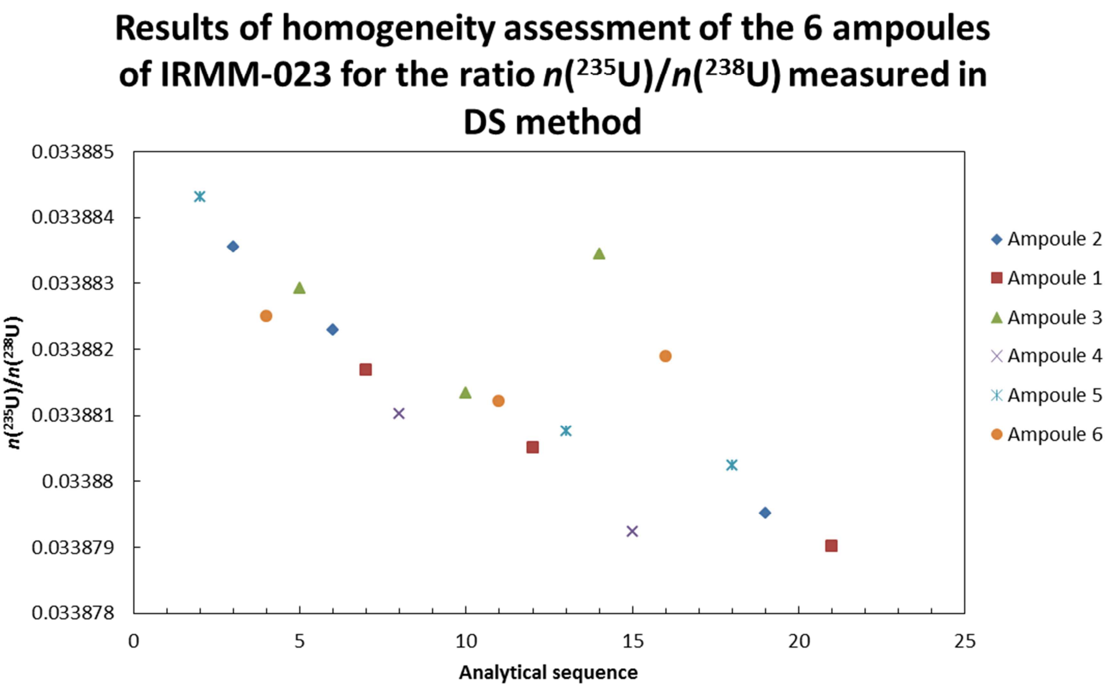
Annex 5.2: Results of homogeneity assessment of the 6 ampoules of IRMM-023 for the ratio $n(^{235}U)/n(^{238}U)$ measured in MTE. Technical outliers are not represented.

Measurements from 1 to 21 were performed on turret 1.

Measurements from 22 to 33 were performed on turret 2.



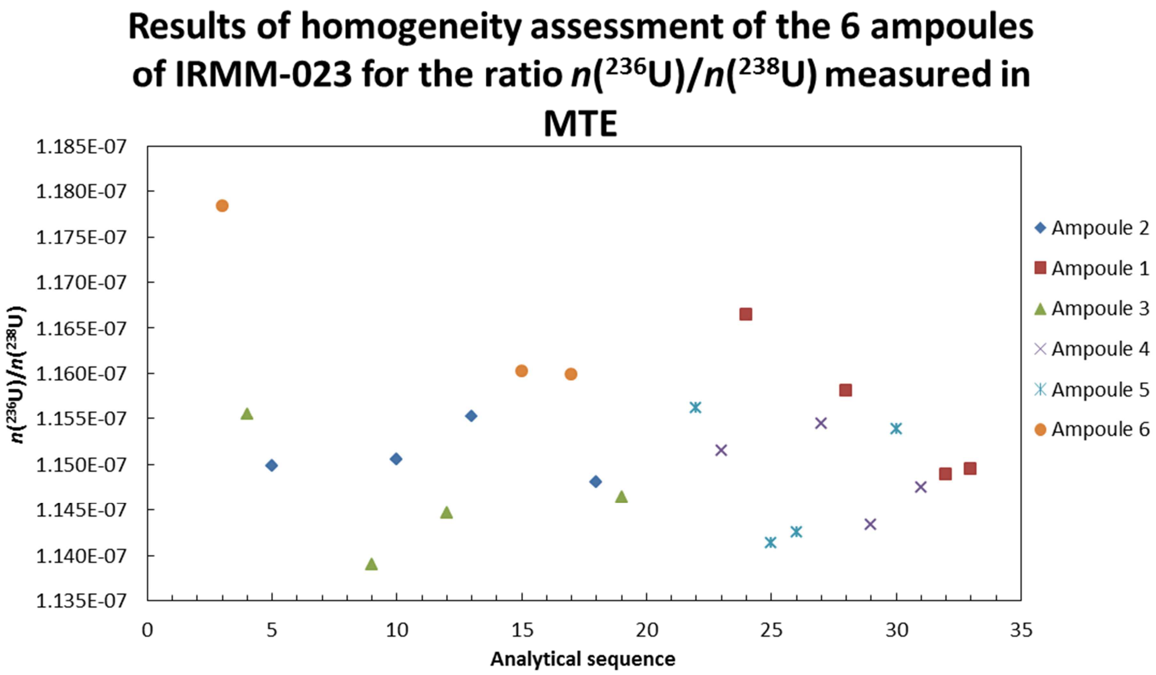
Annex 5.3: Results of homogeneity assessment of the 6 ampoules of IRMM-023 for the ratio $n(^{235}U)/n(^{238}U)$ measured in DS. Technical outliers are not represented.



Annex 5.4: Results of homogeneity assessment of the 6 ampoules of IRMM-023 for the ratio $n(^{236}U)/n(^{238}U)$ measured in MTE. Technical outliers are not represented.

Measurements from 1 to 21 were performed on magazine 1.

Measurements from 22 to 33 were performed on magazine 2.



Annex 6: Certificate of IRMM-058

IRMM

Institute for Reference Materials and Measurements

CERTIFICATE

SPIKE ISOTOPIC REFERENCE MATERIAL IRMM-058

$9.013(12) \cdot 10^{-12}$ mol (^{233}U) $\cdot$ g^{-1} (solution)

The Spike Isotopic Reference Material is supplied with an isotope amount content of ^{233}U certified as above.

The amount of other uranium isotopes present are related to the ^{233}U content through the following certified amount ratios:

$n(^{234}U)/n(^{233}U)$:	0.000 352 4(14)
$n(^{235}U)/n(^{233}U)$:	0.000 004 124(29)
$n(^{236}U)/n(^{233}U)$:	0.000 000 043 4(14)
$n(^{238}U)/n(^{233}U)$:	0.000 010 43(21)

This corresponds to an isotopic composition with the following abundances :

amount fraction (·100)		Mass fraction (·100)	
$n(^{233}U)/n(U)$	99.963 32(14)	$m(^{233}U)/m(U)$	99.963 14(14)
$n(^{234}U)/n(U)$	0.035 22(14)	$m(^{234}U)/m(U)$	0.035 37(14)
$n(^{235}U)/n(U)$	0.000 412 3(29)	$m(^{235}U)/m(U)$	0.000 415 8(29)
$n(^{236}U)/n(U)$	0.000 004 34(14)	$m(^{236}U)/m(U)$	0.000 004 40(14)
$n(^{238}U)/n(U)$	0.001 043(21)	$m(^{238}U)/m(U)$	0.001 065(21)

The molar mass of the uranium in this sample is 233.040 040 4(62) g·mol^{-1}

From the certified values, the following amount content and mass contents are derived:

$9.016(12) \cdot 10^{-12}$	mol (U) $\cdot$ g^{-1} (solution)
$2.100\,4(29) \cdot 10^{-9}$	g (^{233}U) $\cdot$ g^{-1} (solution)
$2.101\,2(29) \cdot 10^{-9}$	g (U) $\cdot$ g^{-1} (solution)

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05/2001

NOTES

1. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor k=2. They apply to the last two digits of the value. The values certified are traceable to the SI.

2. The Spike Isotopic Reference Material IRMM-058 comes in a flame-sealed quartz ampoule containing about 0.050 nmol uranium in 5 mL of a chemically stable nitric acid solution.

3. The molar masses, used in the calculations, are[1]

^{233}U : 233.039 627 0 (60) g·mol^{-1}
^{234}U : 234.040 944 7 (44) g·mol^{-1}
^{235}U : 235.043 922 2 (42) g·mol^{-1}
^{236}U : 236.045 561 0 (42) g·mol^{-1}
^{238}U : 238.050 783 5 (44) g·mol^{-1}

4. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

5. Using this Spike Isotopic Reference Material, the ^{235}U (or ^{238}U) content in an unknown sample can be determined by Isotope Dilution, through a measurement of the isotope amount ratio $R(B) = n(^{233}U)/n(^{235}U)$ in a blend. It should be computed with the aid of the following equation which enables an easy quantification of the uncertainty sources in the procedure :

$$c(^{235}U, X) = \frac{R(Y) - R(B)}{R(B) - R(X)} \cdot \frac{1}{R(Y)} \cdot \frac{m(Y)}{m(X)} \cdot c(^{233}U, Y)$$

$$c(U, X) = \frac{R(Y) - R(B)}{R(B) - R(X)} \cdot \frac{1 + R(X)}{1 + R(Y)} \cdot \frac{m(Y)}{m(X)} \cdot c(U, Y)$$

where:

$R(X)$	=	amount ratio $n(^{233}U)/n(^{235}U)$ in the unknown sample material X
$R(Y)$	=	amount ratio $n(^{233}U)/n(^{235}U)$ in the spike material Y
$m(X)$	=	mass of the unknown sample used in the measurement
$m(Y)$	=	mass of the sample of spike solution used in the measurement
$c(^{235}U, X)$	=	amount content of $^{235}U \cdot kg^{-1}$ sample material
$c(^{233}U, Y)$	=	amount content of $^{233}U \cdot kg^{-1}$ spike solution
$c(U, X)$	=	amount content of $U \cdot kg^{-1}$ sample material
$c(U, Y)$	=	amount content of $U \cdot kg^{-1}$ spike solution.

[1] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation , Nucl Phys A565 (1993) 1-65

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6. This Spike Isotopic Reference Material is traceable to the SI system in the shortest possible way. Measurements calibrated against these Isotopic reference Materials have therefore the potential of being traceable to the SI

The isotopic measurements were performed by A Alonso-Muñoz and H Kühn by Thermal Ionisation Mass Spectrometry and calibrated by means of synthetic uranium isotope mixtures prepared by W Lycke. Chemical preparation of the samples for isotopic measurements was performed by F Kehoe.

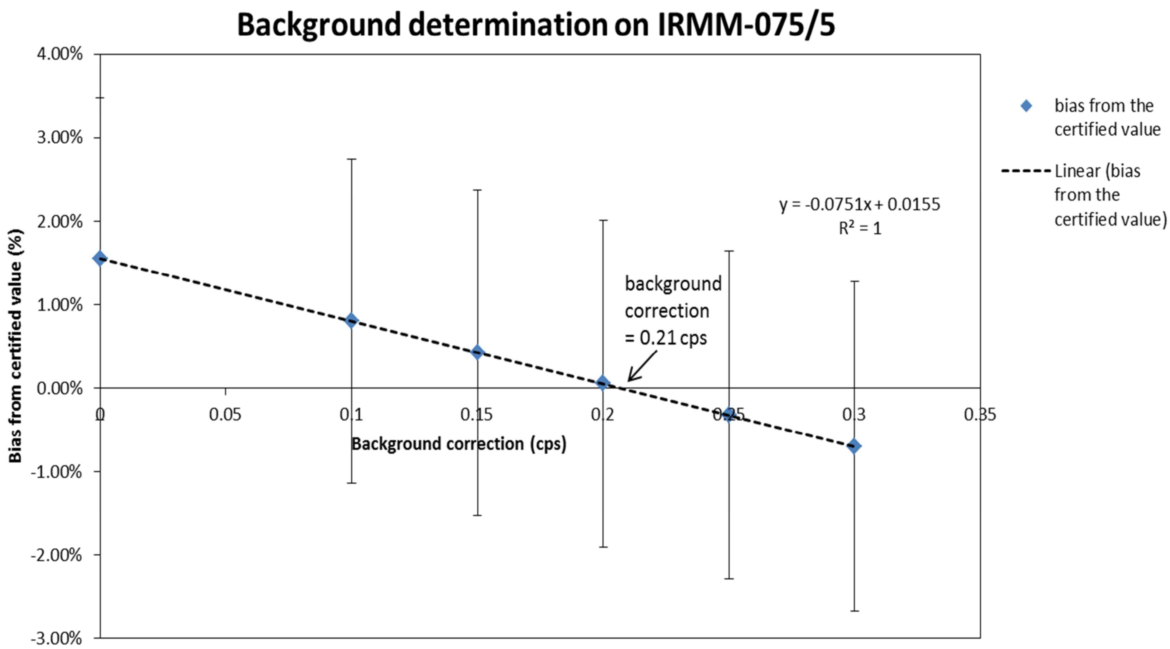
Metrological weighings required in the preparation and certification were performed by F Hendrickx and R Eykens. The ampoulation of this Spike Isotopic Reference Material was accomplished by G Van Baelen A Held and R Eykens.

The overall co-ordination leading to the establishment, certification and issuance of this Spike Isotopic Reference Material was performed by A Verbruggen.

Roger Wellum

B-2440 GEEL May 2001	P Taylor Head Isotope Measurements Unit	R Wellum IRMM Safeguards Coordinator

Annex 7: Background correction determination.



Annex 8: Certificate of IRMM-187

IRMM

Institute for Reference Materials and Measurements

CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-187

$$n(^{233}U)/n(^{238}U) < 0.000\,000\,002$$
$$n(^{234}U)/n(^{238}U) = 0.000\,387\,00(16)$$
$$n(^{235}U)/n(^{238}U) = 0.047\,325(14)$$
$$n(^{236}U)/n(^{238}U) = 0.000\,071\,965(39)$$

The Isotopic Reference Material is supplied with molar ratios certified as above.

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	< 0.000 000 2	$m(^{233}U)/m(U)$	< 0.000 000 2
$n(^{234}U)/n(U)$	0.036 935(15)	$m(^{234}U)/m(U)$	0.036 334(15)
$n(^{235}U)/n(U)$	4.516 7(13)	$m(^{235}U)/m(U)$	4.462 2(13)
$n(^{236}U)/n(U)$	0.006 868 3(37)	$m(^{236}U)/m(U)$	0.006 814 4(36)
$n(^{238}U)/n(U)$	95.439 5(13)	$m(^{238}U)/m(U)$	95.494 7(13)

The molar mass of the uranium in this sample is 237.913 355(40) $g{\cdot}mol^{-1}$

NOTES

1. All uncertainties indicated are expanded uncertainties $U = k{\cdot}u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor $k = 2$. They apply to the last two digits of the value. The values certified are traceable to the SI through gravimetrically prepared standards.

2. The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

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3. The Isotopic Reference Material IRMM-187 comes in a flame-sealed glass ampoule containing about 0.004 mol uranium in 5 mL of a chemically stable nitric acid solution. The molality is about 6 m HNO_3 (i.e. 6 mol HNO_3 kg^{-1} of solvent); the molarity is 5 M HNO_3 (i.e. 5 mol $HNO_3 \cdot L^{-1}$ of solution).

4. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

5. The atomic masses, used in the calculations, are[1]

^{233}U: 233.039 627 0(60) $g \cdot mol^{-1}$
^{234}U: 234.040 944 7(44) $g \cdot mol^{-1}$
^{235}U: 235.043 922 2(42) $g \cdot mol^{-1}$
^{236}U: 236.045 561 0(42) $g \cdot mol^{-1}$
^{238}U: 238.050 783 5(44) $g \cdot mol^{-1}$

Chemical preparation and ampoulation of this Isotopic Reference Material were accomplished by W Lycke and A Verbruggen.

Mass spectrometric measurements were performed by W De Bolle for the $[n(^{235}U)/n(^{238}U)]$ isotope ratio using the MAT511 mass spectrometer on UF_6 samples prepared by W De Bolle. TIMS re-measurements on $[n(^{234}U)/n(^{238}U)]$ and $[n(^{236}U)/n(^{238}U)]$ were performed by S Richter using the TRITON mass spectrometer. Sample ampoules were re-opened and sample solutions prepared for TIMS analysis by A Alonso[2]. A Verbruggen was responsible for the preparation and issuance of the certificate.

Metrological weighing required in the preparation was performed by F Hendrickx.

B-2440 GEEL	P Taylor	R Wellum
December 1987	Head	IRMM Safeguards Coordinator
	Isotope Measurements Unit	

Revised July 1993
Revised June 1999
Revised March 2005

1 G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
2 Measurement certificate IM/MeaC/27/04-IRMM-187 of March 2005

Annex 9: Certificate of IRMM-183

IRMM

Institute for Reference Materials and Measurements

CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-183

$$n(^{233}U)/n(^{238}U) < 0.000\,000\,002$$
$$n(^{234}U)/n(^{238}U) = 0.000\,019\,755(22)$$
$$n(^{235}U)/n(^{238}U) = 0.003\,215\,7(16)$$
$$n(^{236}U)/n(^{238}U) = 0.000\,148\,358(54)$$

The Isotopic Reference Material is supplied with molar ratios certified as above.

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	< 0.000 000 2	$m(^{233}U)/m(U)$	< 0.000 000 2
$n(^{234}U)/n(U)$	0.001 968 8(22)	$m(^{234}U)/m(U)$	0.001 935 8(22)
$n(^{235}U)/n(U)$	0.320 49(16)	$m(^{235}U)/m(U)$	0.316 45(16)
$n(^{236}U)/n(U)$	0.014 785 8(54)	$m(^{236}U)/m(U)$	0.014 661 8(54)
$n(^{238}U)/n(U)$	99.662 76(17)	$m(^{238}U)/m(U)$	99.666 95(16)

The molar mass of the uranium in this sample is 238.040 771 5(66) $g \cdot mol^{-1}$

NOTES

1. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor $k = 2$. They apply to the last two digits of the value. The values certified are traceable to the SI through gravimetrically prepared standards.

2. The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

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3. The Isotopic Reference Material IRMM-183 comes in a flame-sealed glass ampoule containing about 0.004 mol uranium in 5 mL of a chemically stable nitric acid solution. The molality is about 6 m HNO_3 (i.e. 6 mol HNO_3 kg^{-1} of solvent); the molarity is 5 M HNO_3 (i.e. 5 mol $HNO_3 \cdot L^{-1}$ of solution).

4. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

5. The atomic masses, used in the calculations, are[1]

^{233}U: 233.039 627 0(60) $g \cdot mol^{-1}$
^{234}U: 234.040 944 7(44) $g \cdot mol^{-1}$
^{235}U: 235.043 922 2(42) $g \cdot mol^{-1}$
^{236}U: 236.045 561 0(42) $g \cdot mol^{-1}$
^{238}U: 238.050 783 5(44) $g \cdot mol^{-1}$

Chemical preparation and ampoulation of this Isotopic Reference Material were accomplished by W Lycke and A Verbruggen.

Mass spectrometric measurements were performed by W De Bolle for the $[n(^{235}U)/n(^{238}U)]$ isotope ratio using the MAT511 mass spectrometer on UF_6 samples prepared by W De Bolle. TIMS re-measurements on $[n(^{234}U)/n(^{238}U)]$ and $[n(^{236}U)/n(^{238}U)]$ were performed by S Richter using the TRITON mass spectrometer. Sample ampoules were re-opened and sample solutions prepared for TIMS analysis by A Alonso[2]. A Verbruggen was responsible for the preparation and issuance of the certificate.

Metrological weighing required in the preparation was performed by F Hendrickx.

Roger Wellum

B-2440 GEEL December 1987	P Taylor Head Isotope Measurements Unit	R Wellum IRMM Safeguards Coordinator

Revised July 1993
Revised June 1999
Revised March 2005

[1] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[2] Measurement certificate IM/MeaC/23/04-IRMM-183 of March 2005

Annex 10: Certificate of IRMM-184

IRMM

Institute for Reference Materials and Measurements

CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-184

$$n(^{233}U)/n(^{238}U) < 0.000\,000\,002$$
$$n(^{234}U)/n(^{238}U) = 0.000\,053\,138(32)$$
$$n(^{235}U)/n(^{238}U) = 0.007\,262\,3(22)$$
$$n(^{236}U)/n(^{238}U) = 0.000\,000\,124\,46(17)$$

The Isotopic Reference Material is supplied with molar ratios certified as above.

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	< 0.000 000 2	$m(^{233}U)/m(U)$	< 0.000 000 2
$n(^{234}U)/n(U)$	0.005 275 2(32)	$m(^{234}U)/m(U)$	0.005 186 8(32)
$n(^{235}U)/n(U)$	0.720 96(21)	$m(^{235}U)/m(U)$	0.711 91(21)
$n(^{236}U)/n(U)$	0.000 012 356(17)	$m(^{236}U)/m(U)$	0.000 012 253(17)
$n(^{238}U)/n(U)$	99.273 76(22)	$m(^{238}U)/m(U)$	99.282 89(21)

The molar mass of the uranium in this sample is 238.028 893 6(79) $g \cdot mol^{-1}$

NOTES

1. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor k = 2. They apply to the last two digits of the value. The values certified are traceable to the SI through gravimetrically prepared standards.

2. The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

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3. The Isotopic Reference Material IRMM-184 comes in a flame-sealed glass ampoule containing about 0.004 mol uranium in 5 mL of a chemically stable nitric acid solution. The molality is about 6 m HNO_3 (i.e. 6 mol HNO_3 kg^{-1} of solvent); the molarity is 5 M HNO_3 (i.e. 5 mol $HNO_3 \cdot L^{-1}$ of solution).

4. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safehandling of radioactive materials.

5. The atomic masses, used in the calculations, are[1]

^{233}U: 233.039 627 0(60) $g \cdot mol^{-1}$
^{234}U: 234.040 944 7(44) $g \cdot mol^{-1}$
^{235}U: 235.043 922 2(42) $g \cdot mol^{-1}$
^{236}U: 236.045 561 0(42) $g \cdot mol^{-1}$
^{238}U: 238.050 783 5(44) $g \cdot mol^{-1}$

Chemical preparation and ampoulation of this Isotopic Reference Material were accomplished by W Lycke and A Verbruggen.

Mass spectrometric measurements were performed by W De Bolle for the $[n(^{235}U)/n(^{238}U)]$ isotope ratio using the MAT511 mass spectrometer on UF_6 samples prepared by W De Bolle. TIMS re-measurements on $[n(^{234}U)/n(^{238}U)]$ and $[n(^{236}U)/n(^{238}U)]$ were performed by S Richter using the TRITON mass spectrometer. Sample ampoules were re-opened and sample solutions prepared for TIMS analysis by A Alonso[2]. A Verbruggen was responsible for the preparation and issuance of the certificate.

Metrological weighing required in the preparation was performed by F Hendrickx.

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	Isotope Measurements Unit	

Revised July 1993
Revised June 1999
Revised March 2005

[1] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[2] Measurement certificate IM/MeaC/24/04-IRMM-184 of March 2005

Annex 11: Certificate of IRMM-186

IRMM

Institute for Reference Materials and Measurements

CERTIFICATE
ISOTOPIC REFERENCE MATERIAL IRMM-186

$$n(^{233}U)/n(^{238}U) < 0.000\,000\,002$$
$$n(^{234}U)/n(^{238}U) = 0.000\,293\,65(13)$$
$$n(^{235}U)/n(^{238}U) = 0.030\,771\,1(92)$$
$$n(^{236}U)/n(^{238}U) = 0.000\,033\,219(23)$$

The Isotopic Reference Material is supplied with molar ratios certified as above.

This corresponds to an isotopic composition with the following abundances:

amount fraction (·100)		mass fraction (·100)	
$n(^{233}U)/n(U)$	< 0.000 000 2	$m(^{233}U)/m(U)$	< 0.000 000 2
$n(^{234}U)/n(U)$	0.028 479(12)	$m(^{234}U)/m(U)$	0.028 010(12)
$n(^{235}U)/n(U)$	2.984 30(87)	$m(^{235}U)/m(U)$	2.947 73(86)
$n(^{236}U)/n(U)$	0.003 221 7(22)	$m(^{236}U)/m(U)$	0.003 195 8(22)
$n(^{238}U)/n(U)$	96.983 99(88)	$m(^{238}U)/m(U)$	97.021 07(87)

The molar mass of the uranium in this sample is 237.959 843(27) $g \cdot mol^{-1}$

NOTES

1. All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement. They are given in parentheses and include a coverage factor k = 2. They apply to the last two digits of the value. The values certified are traceable to the SI through gravimetrically prepared standards.

2. The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

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3. The Isotopic Reference Material IRMM-186 comes in a flame-sealed glass ampoule containing about 0.004 mol uranium in 5 mL of a chemically stable nitric acid solution. The molality is about 6 m HNO_3 (i.e. 6 mol HNO_3 kg^{-1} of solvent); the molarity is 5 M HNO_3 (i.e. 5 mol $HNO_3 \cdot L^{-1}$ of solution).

4. The ampoule should be handled with great care and by experienced personnel in a laboratory environment suitably equipped for the safe handling of radioactive materials.

5. The atomic masses, used in the calculations, are[1]

^{233}U: 233.039 627 0(60) $g \cdot mol^{-1}$
^{234}U: 234.040 944 7(44) $g \cdot mol^{-1}$
^{235}U: 235.043 922 2(42) $g \cdot mol^{-1}$
^{236}U: 236.045 561 0(42) $g \cdot mol^{-1}$
^{238}U: 238.050 783 5(44) $g \cdot mol^{-1}$

Chemical preparation and ampoulation of this Isotopic Reference Material were accomplished by W Lycke and A Verbruggen.

Mass spectrometric measurements were performed by W De Bolle for the $[n(^{235}U)/n(^{238}U)]$ isotope ratio using the MAT511 mass spectrometer on UF_6 samples prepared by W De Bolle. TIMS re-measurements on $[n(^{234}U)/n(^{238}U)]$ and $[n(^{236}U)/n(^{238}U)]$ were performed by S Richter using the TRITON mass spectrometer. Sample ampoules were re-opened and sample solutions prepared for TIMS analysis by A Alonso[2]. A Verbruggen was responsible for the preparation and issuance of the certificate.

Metrological weighing required in the preparation was performed by F Hendrickx.

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Head
Isotope Measurements Unit

R Wellum
IRMM Safeguards Coordinator

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[1] G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation, Nucl Phys A565 (1993) 1-65.
[2] Measurement certificate IM/MeaC/26/04-IRMM-186 of March 2005

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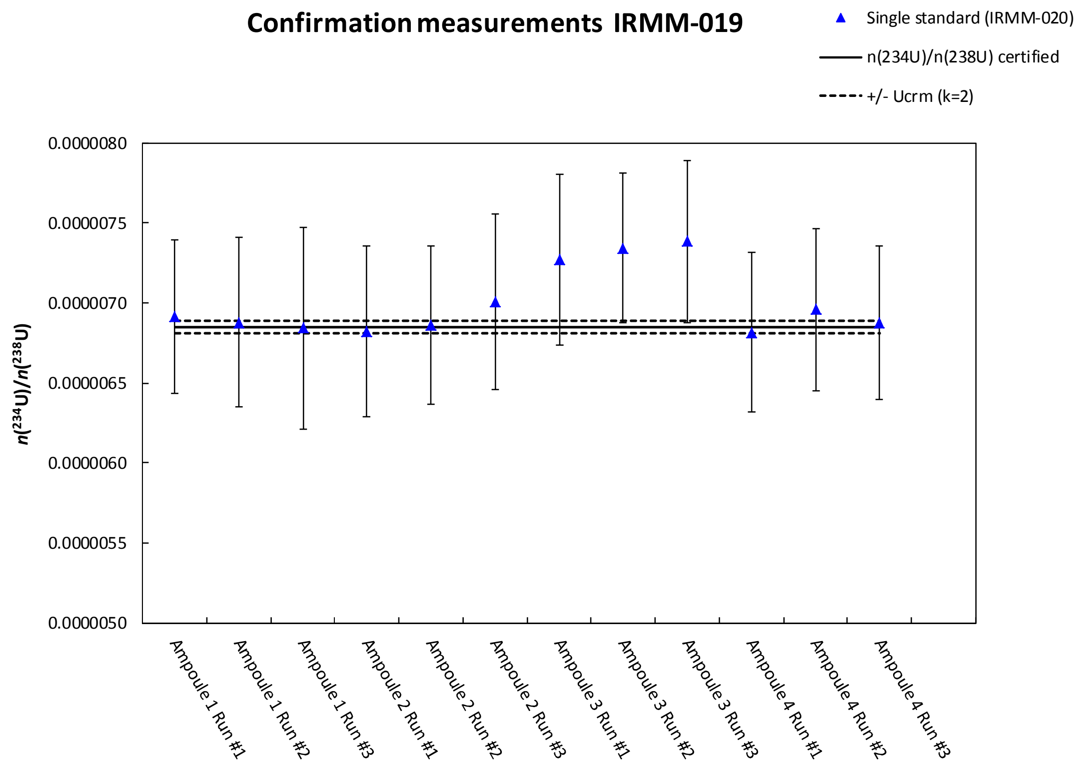
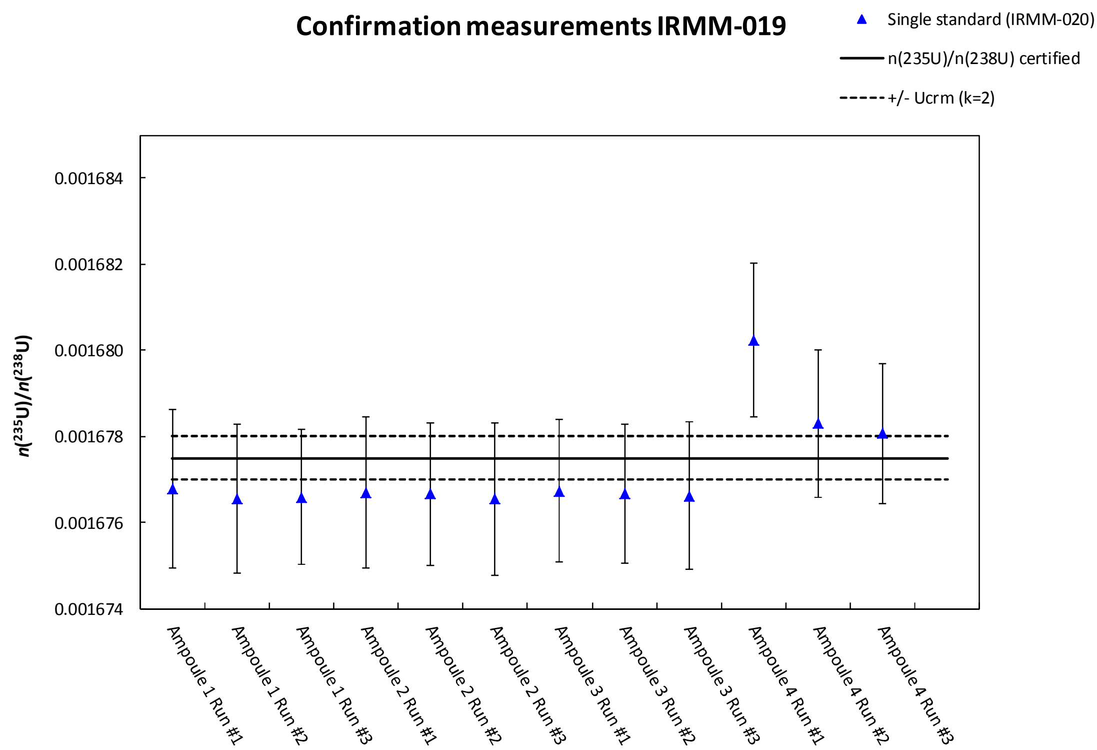
Annex 12: Confirmation measurements by UF_6 GSMS

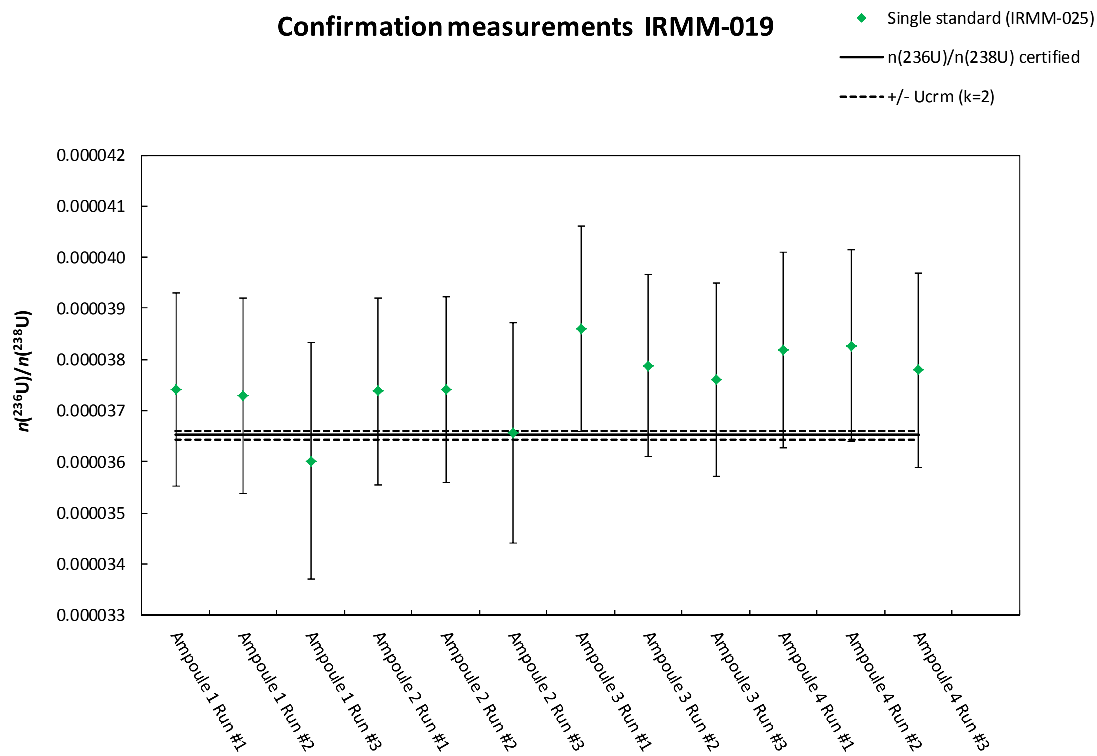
Legend:

Filled triangles represent the measurements corrected using the "single standard method" with the lower enriched uranium reference material, diamonds represent the measurements corrected using the "single standard method" with the higher enriched uranium reference material. Squares represent the measurement calculated using the MCDS method. The corrections for GSMS measurements are described in detail in reference [12] of the certification report.

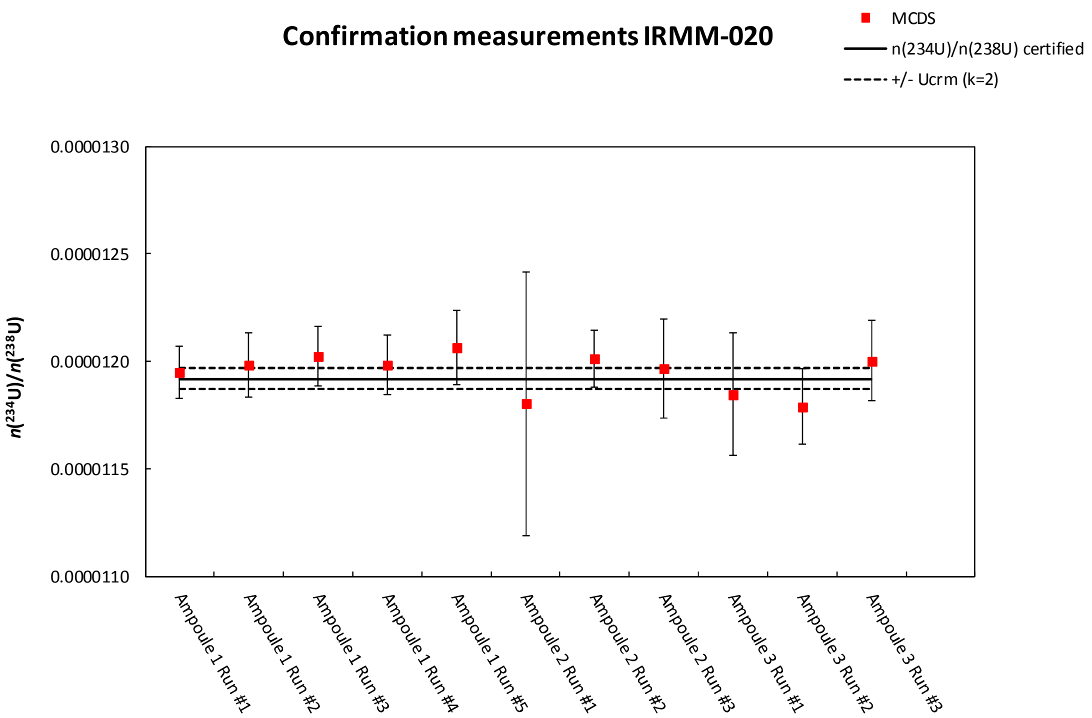
Annex 12.1: Confirmation measurements for IRMM-019

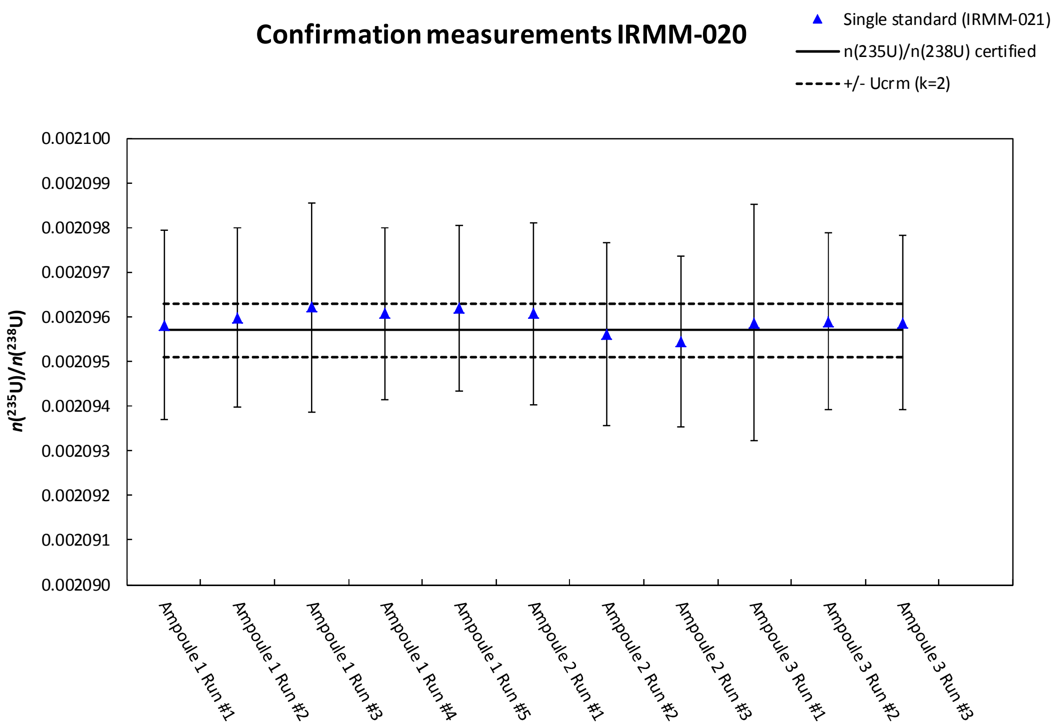


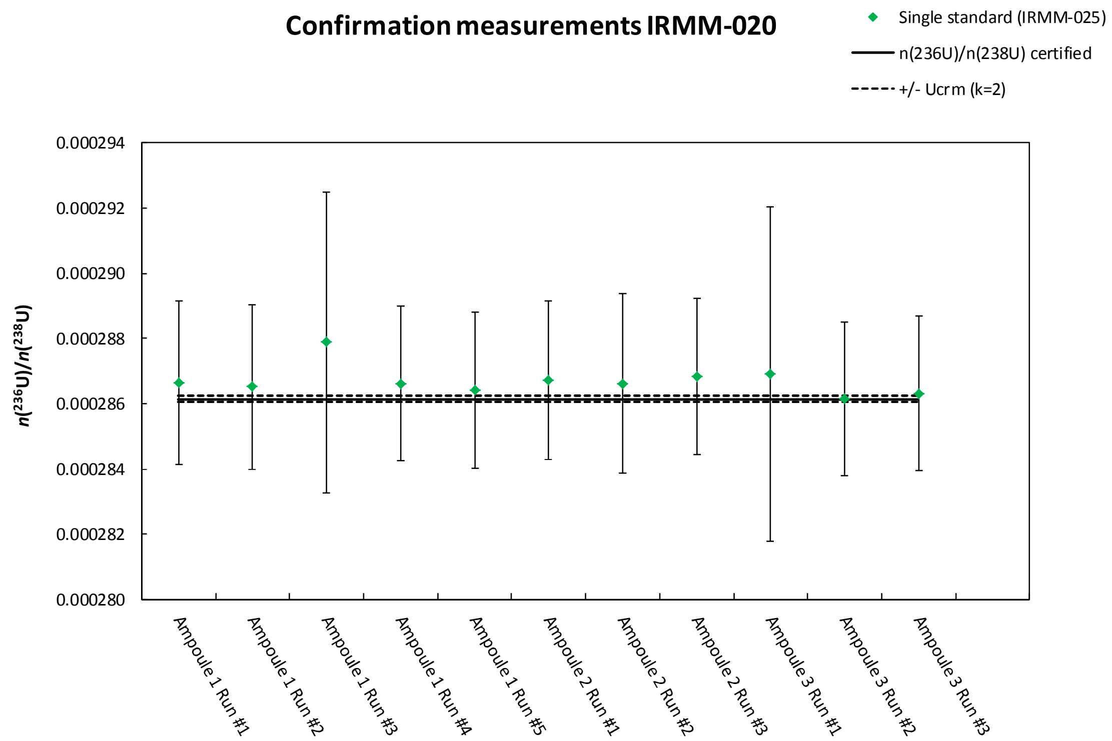

Confirmation measurements IRMM-019
Single standard (IRMM-020)
n(235U)/n(238U) certified
+/- Ucrm (k=2)
$n(^{235}U)/n(^{238}U)$
0.001684
0.001682
0.001680
0.001678
0.001676
0.001674
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3
Ampoule 4 Run #1
Ampoule 4 Run #2
Ampoule 4 Run #3


Confirmation measurements IRMM-019
Single standard (IRMM-025)
n(236U)/n(238U) certified
+/- Ucrm (k=2)
$n(^{236}U)/n(^{238}U)$
0.000042
0.000041
0.000040
0.000039
0.000038
0.000037
0.000036
0.000035
0.000034
0.000033
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3
Ampoule 4 Run #1
Ampoule 4 Run #2
Ampoule 4 Run #3

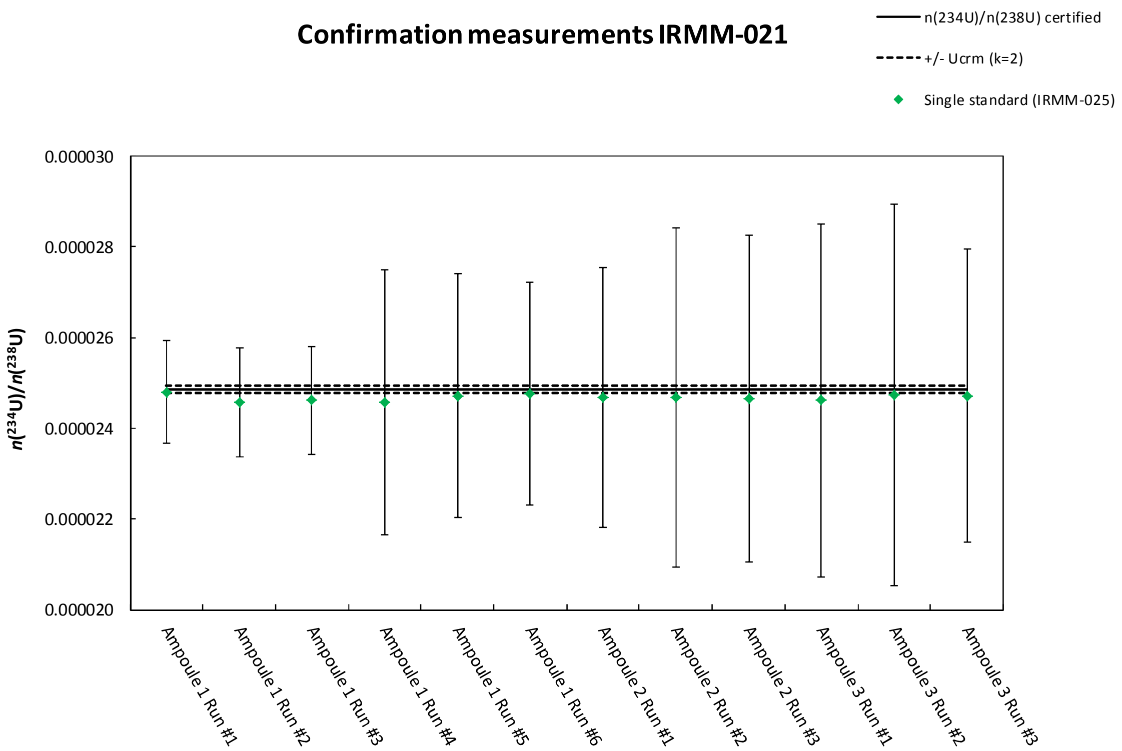
Annex 12.2: Confirmation measurements for IRMM-020

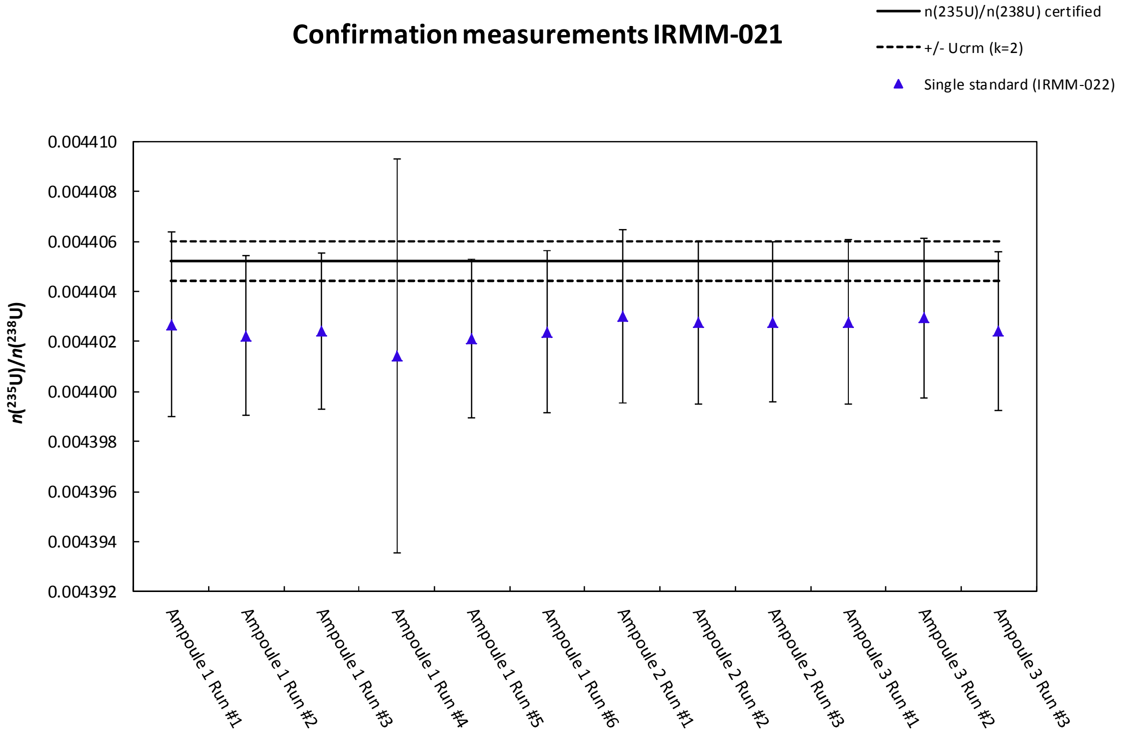






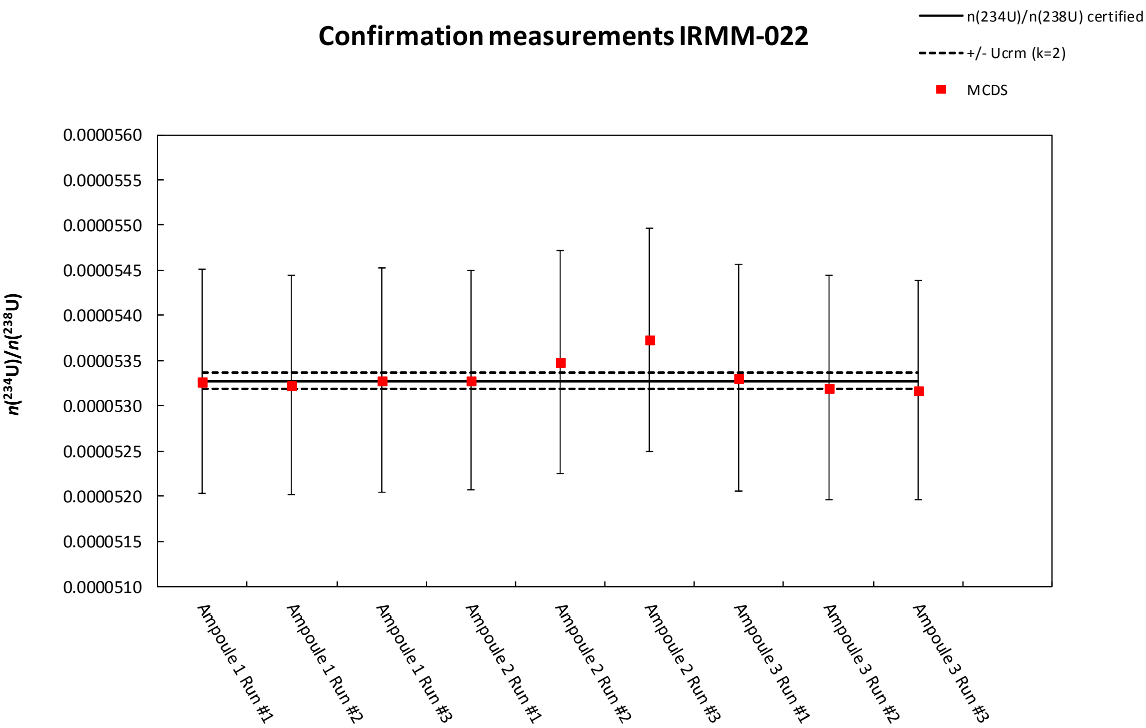
Annex 12.3: Confirmation measurements for IRMM-021

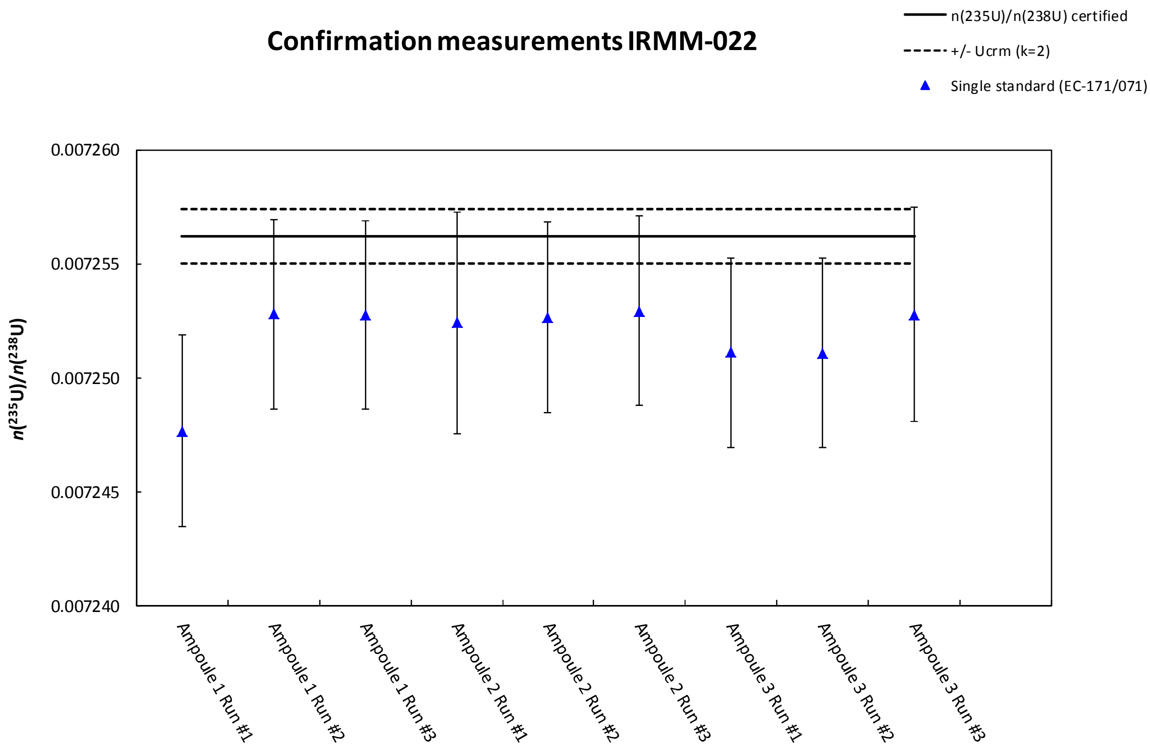




$n(^{236}U)/n(^{238}U)$ is below the detection limit of the technique (<0.000005)

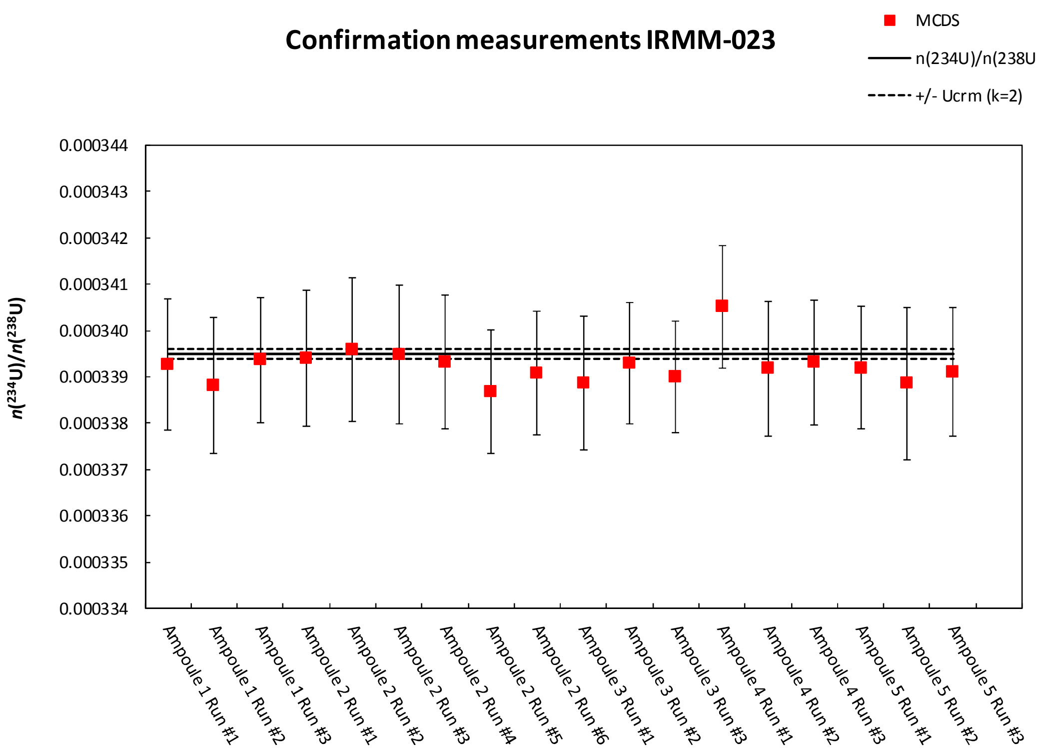
Annex 12.4: Confirmation measurements for IRMM-022

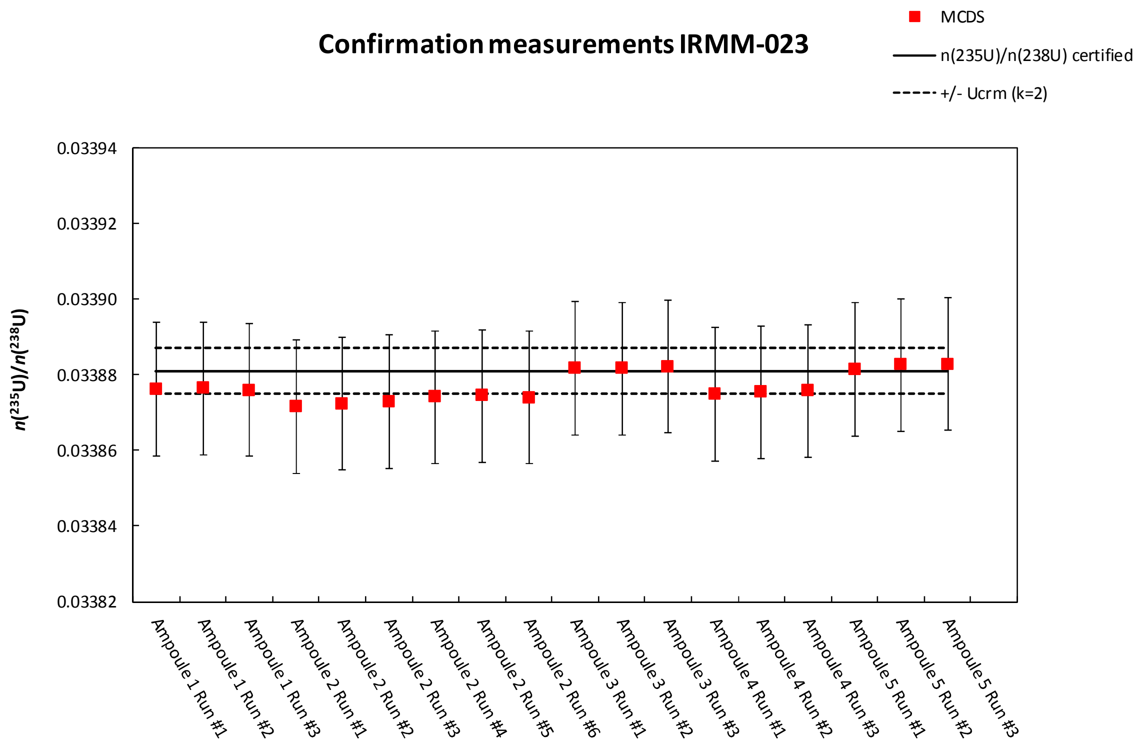




$n(^{236}U)/n(^{238}U)$ is below the detection limit of the technique (<0.000005)

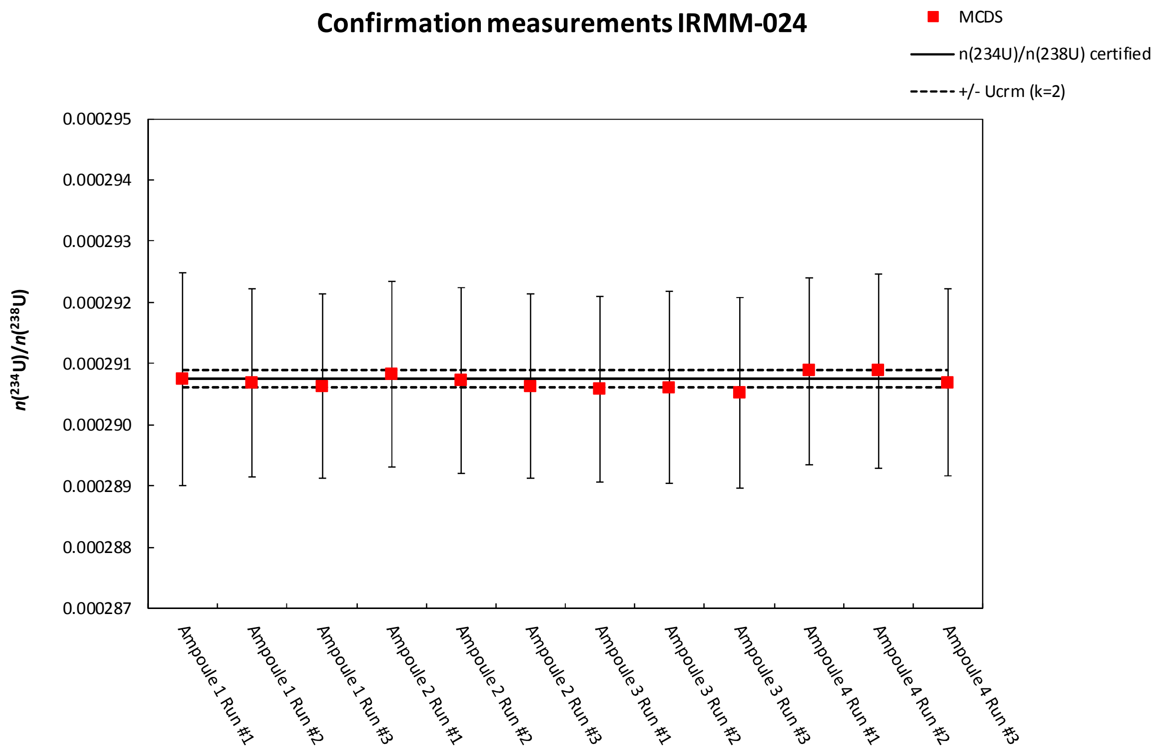
Annex 12.5: Confirmation measurements for IRMM-023

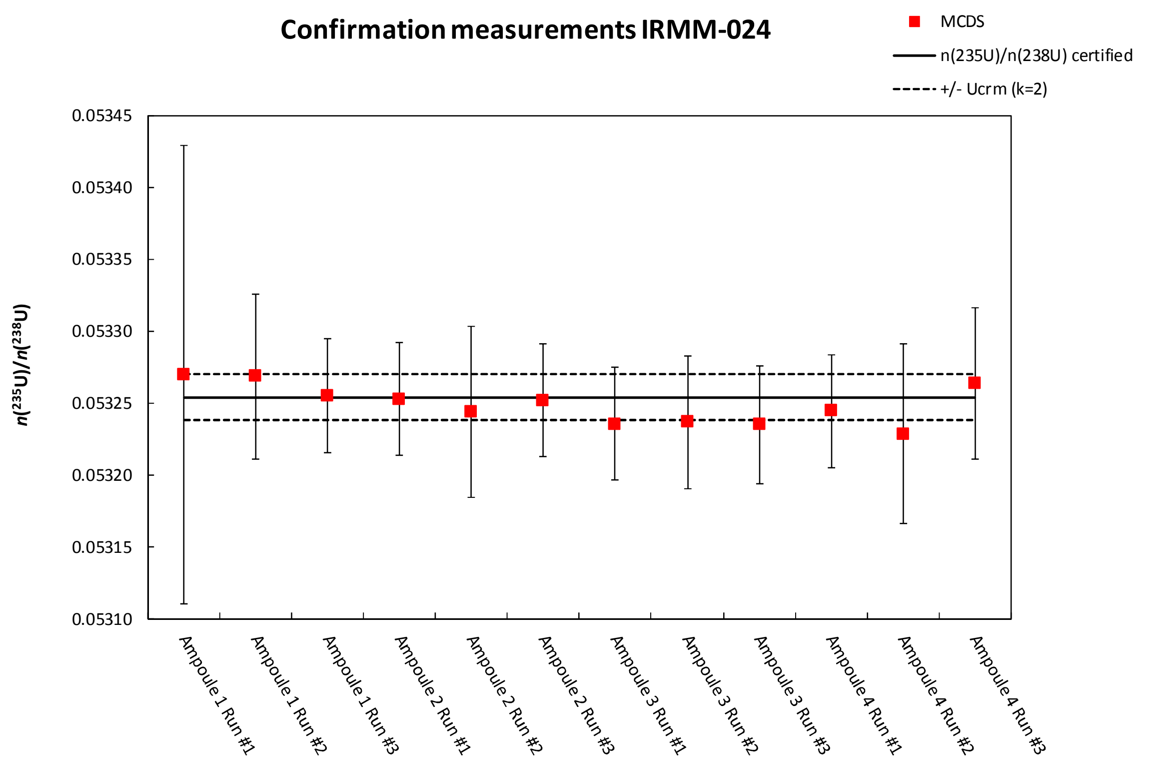




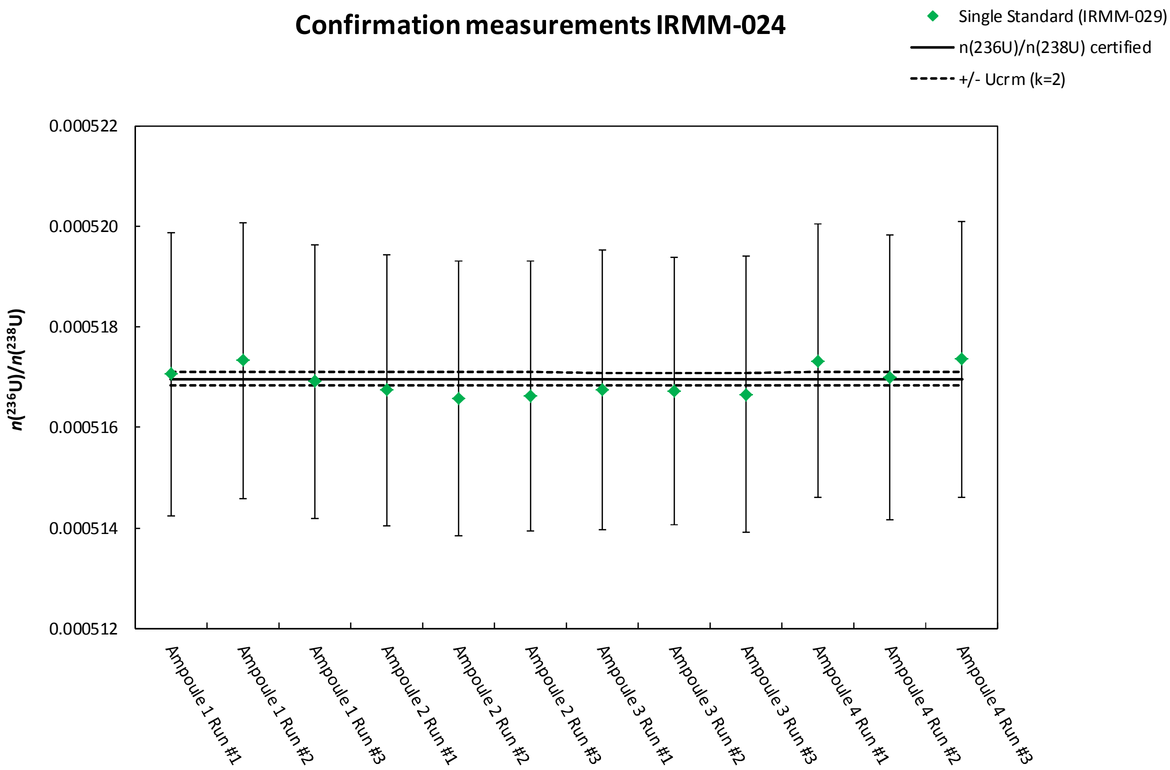
$n(^{236}U)/n(^{238}U)$ is below the detection limit of the technique (<0.000005)

Annex 12.6: Confirmation measurements for IRMM-024



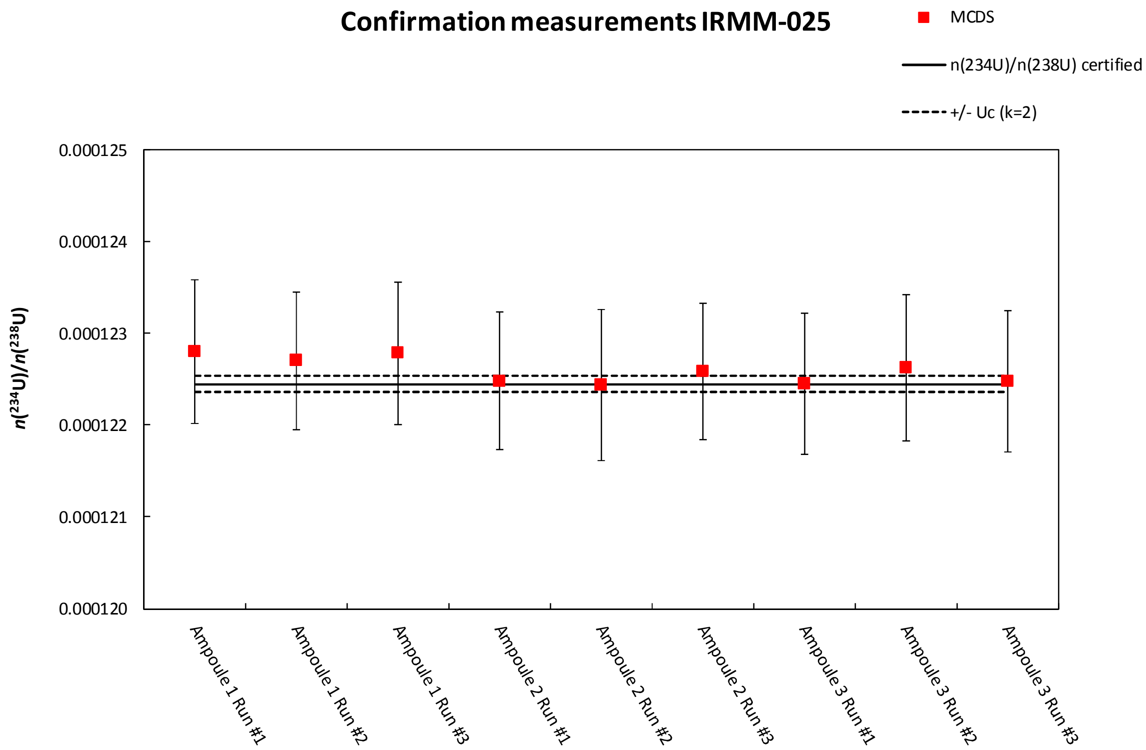


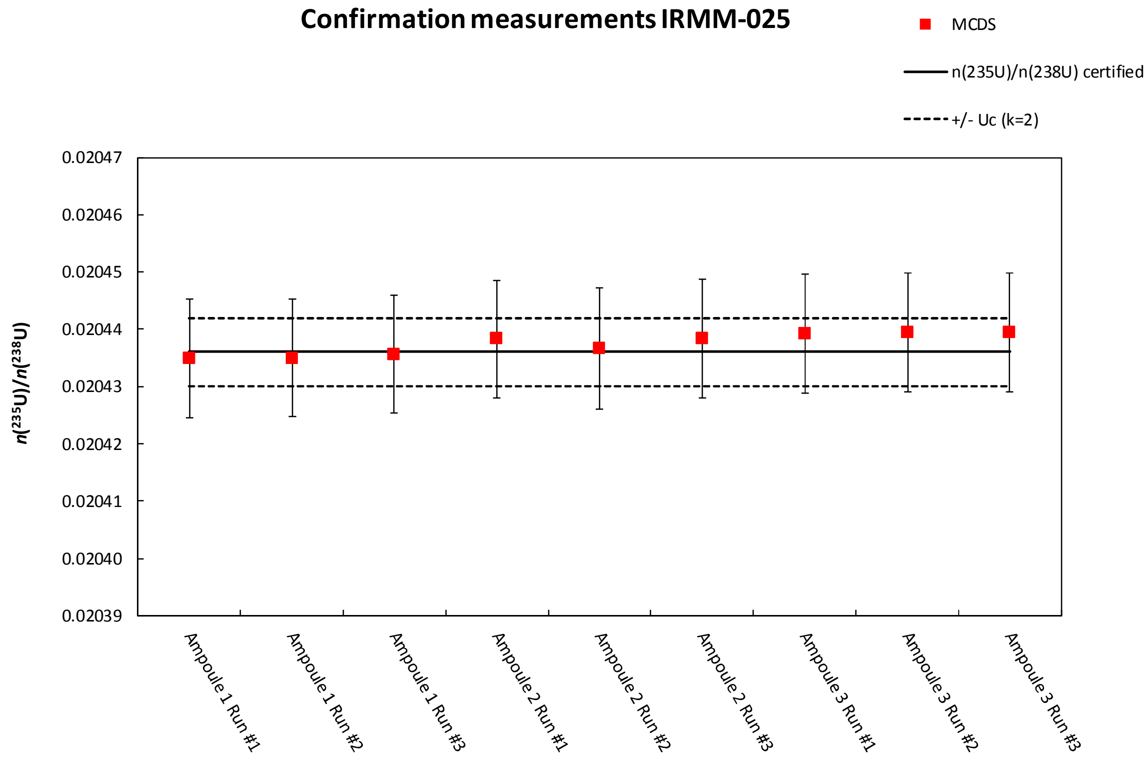
Confirmation measurements IRMM-024
MCDS
n(235U)/n(238U) certified
+/- Ucrm (k=2)
0.05345
0.05340
0.05335
0.05330
0.05325
0.05320
0.05315
0.05310
n(235U)/n(238U)
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3
Ampoule 4 Run #1
Ampoule 4 Run #2
Ampoule 4 Run #3

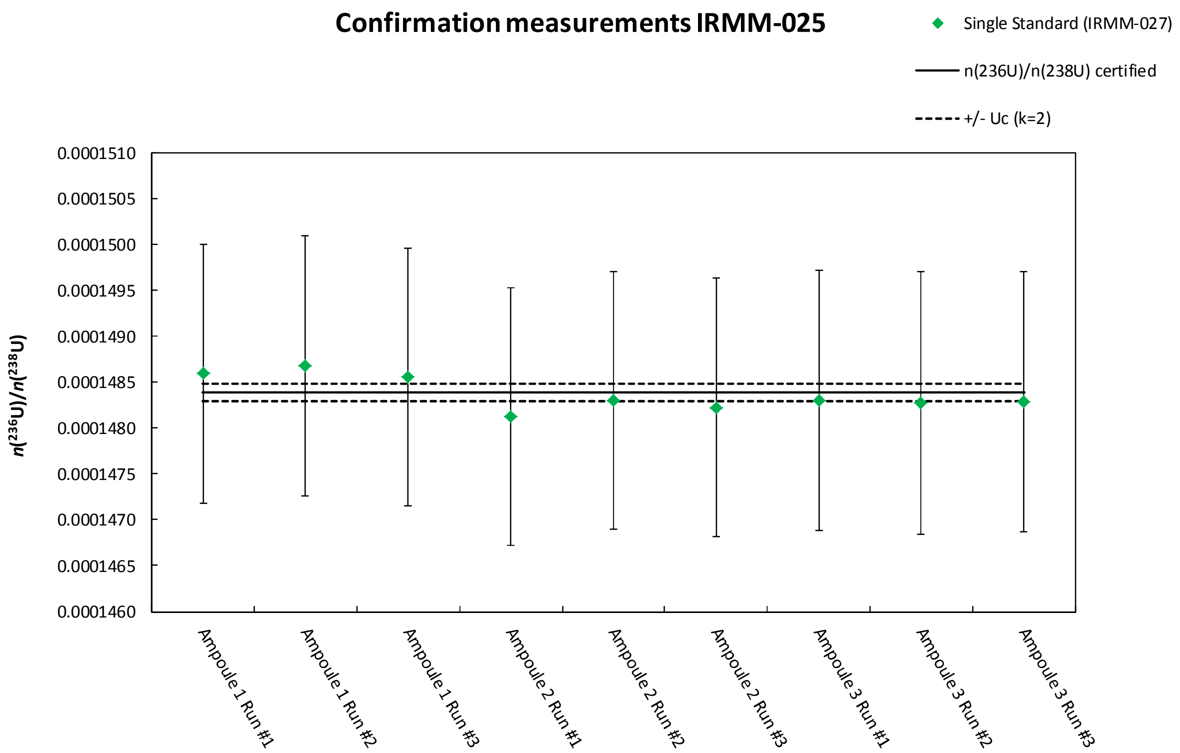


Confirmation measurements IRMM-024
Single Standard (IRMM-029)
n(236U)/n(238U) certified
+/- Ucrm (k=2)
0.000522
0.000520
0.000518
0.000516
0.000514
0.000512
n(236U)/n(238U)
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3
Ampoule 4 Run #1
Ampoule 4 Run #2
Ampoule 4 Run #3

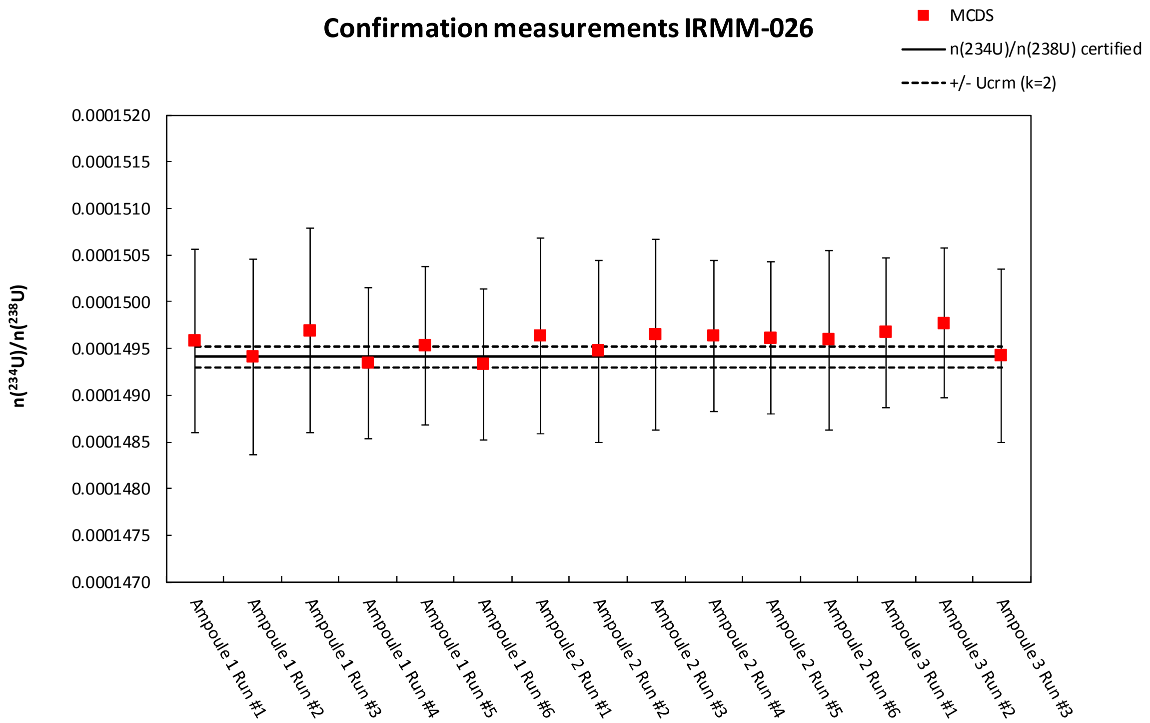
Annex 12.7: Confirmation measurements for IRMM-025

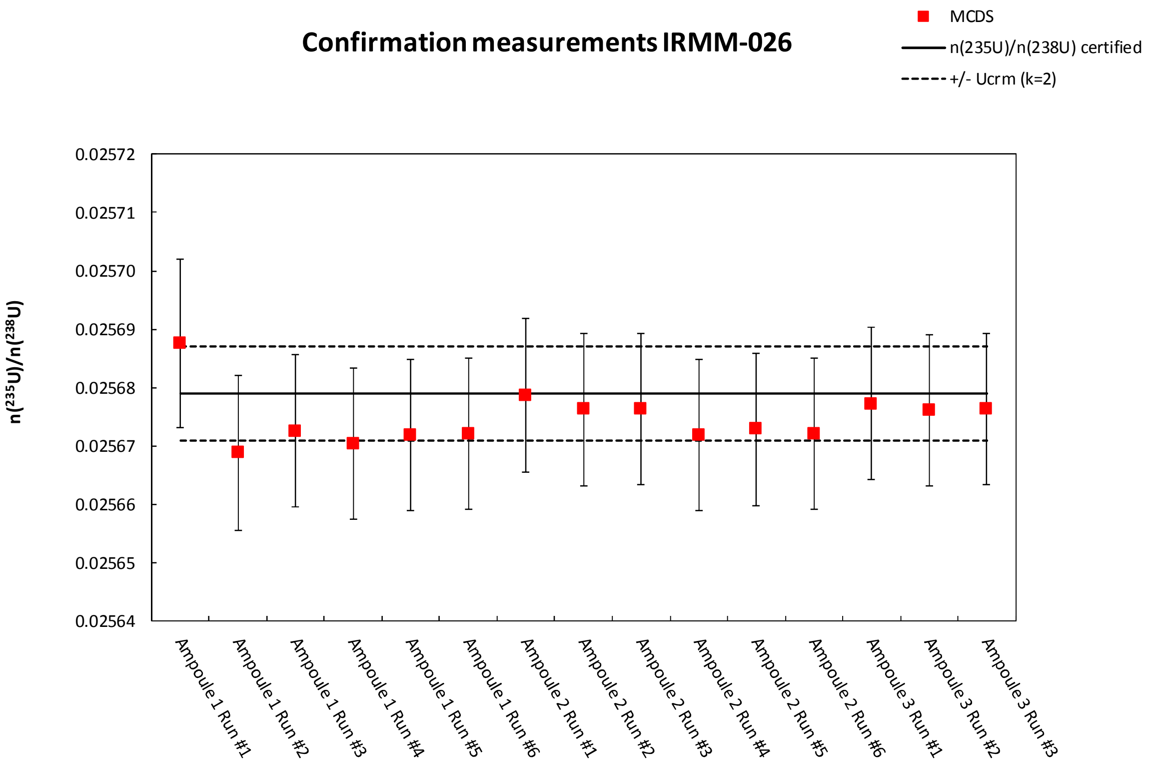


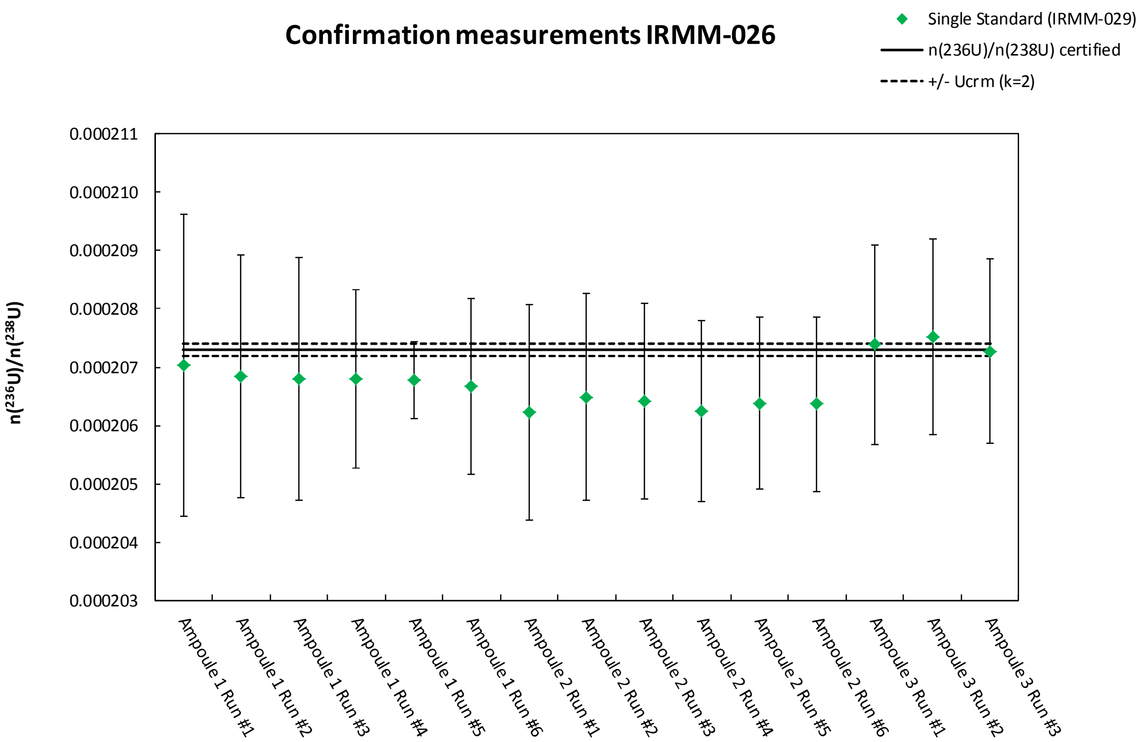




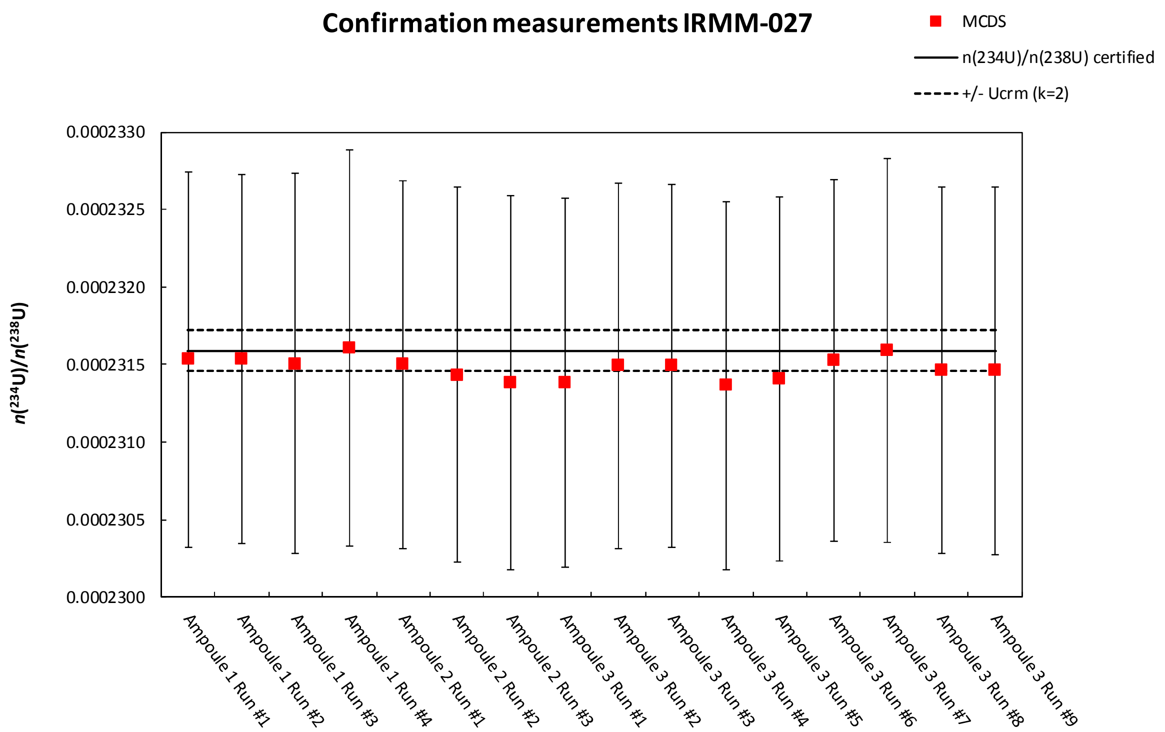
Annex 12.8: Confirmation measurements for IRMM-026

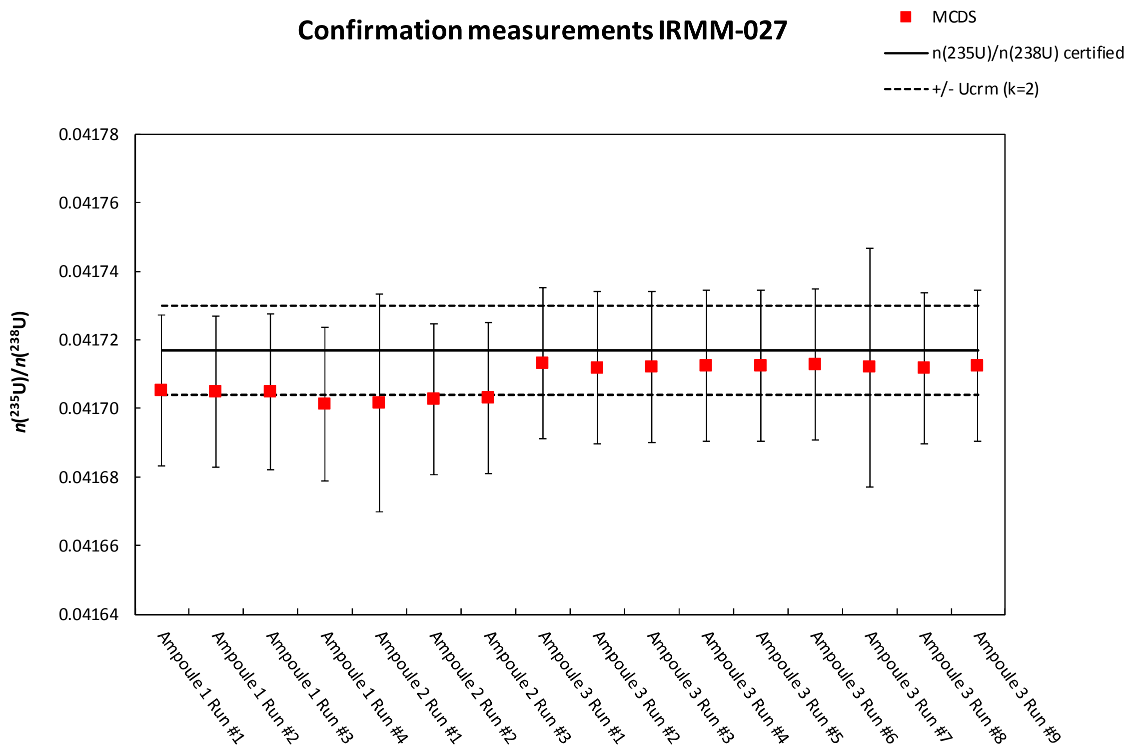


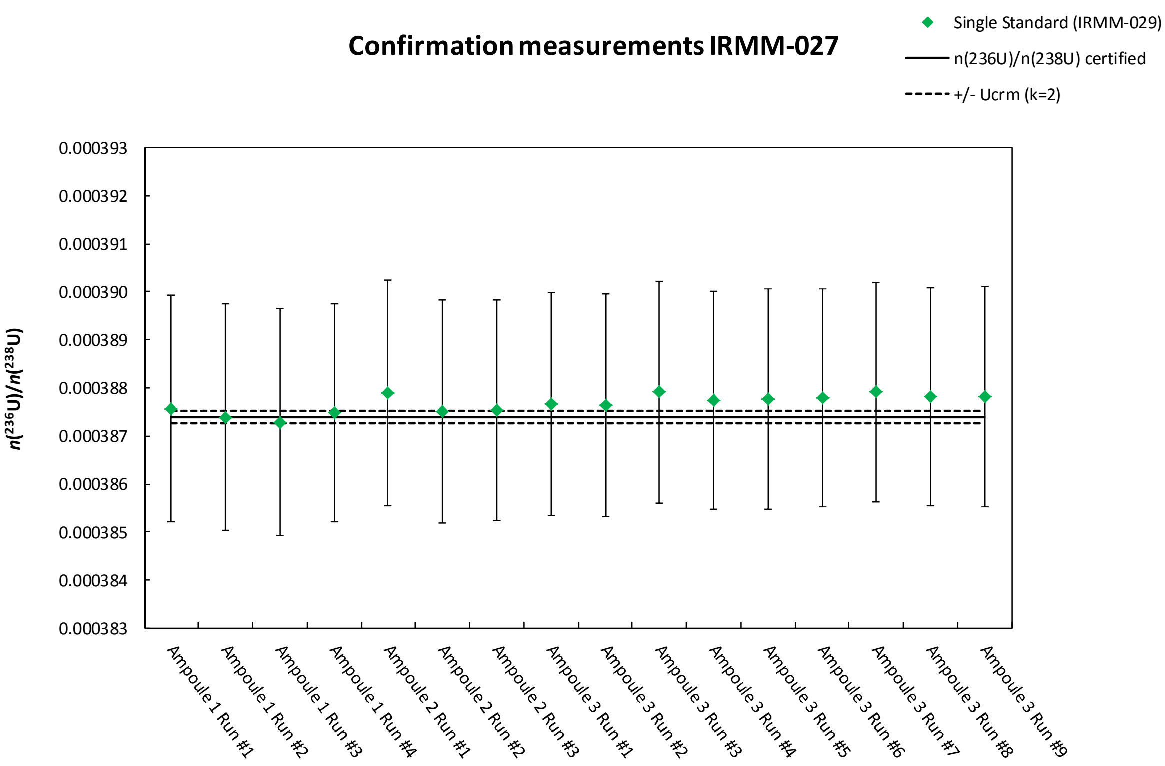

Confirmation measurements IRMM-026
MCDS
n(235U)/n(238U) certified
+/- Ucrm (k=2)
n(235U)/n(238U)
0.02572
0.02571
0.02570
0.02569
0.02568
0.02567
0.02566
0.02565
0.02564
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 1 Run #4
Ampoule 1 Run #5
Ampoule 1 Run #6
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 2 Run #4
Ampoule 2 Run #5
Ampoule 2 Run #6
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3


Confirmation measurements IRMM-026
Single Standard (IRMM-029)
n(236U)/n(238U) certified
+/- Ucrm (k=2)
n(236U)/n(238U)
0.000211
0.000210
0.000209
0.000208
0.000207
0.000206
0.000205
0.000204
0.000203
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 1 Run #4
Ampoule 1 Run #5
Ampoule 1 Run #6
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 2 Run #4
Ampoule 2 Run #5
Ampoule 2 Run #6
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3

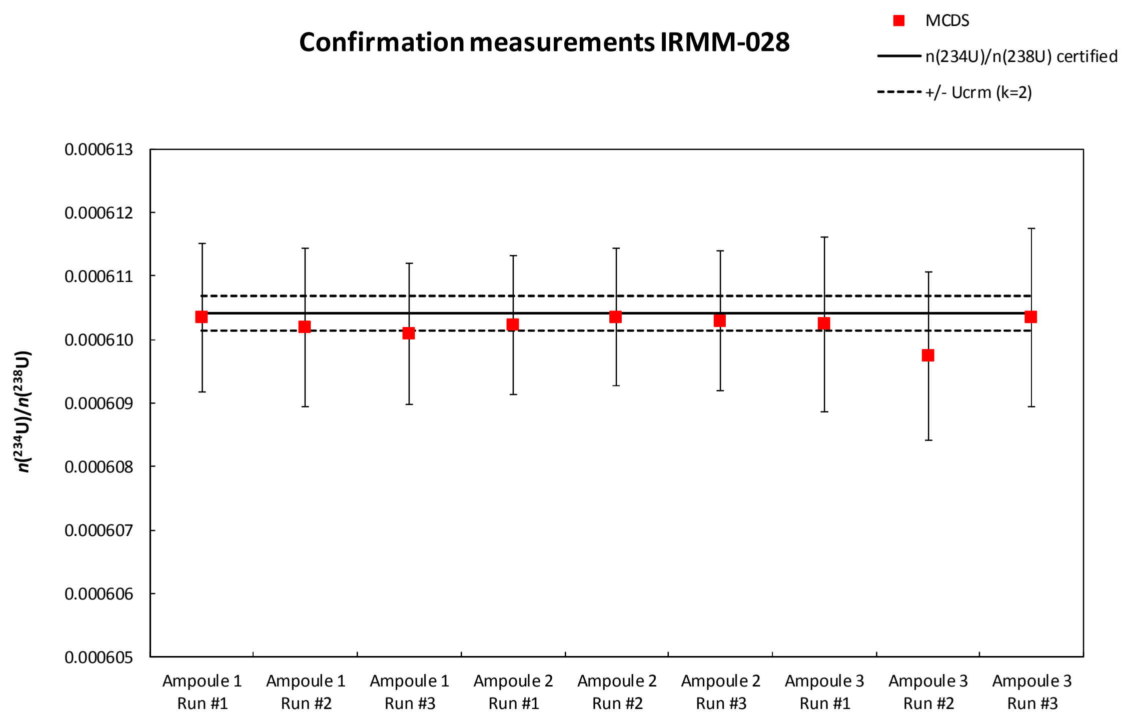
Annex 12.9: Confirmation measurements for IRMM-027

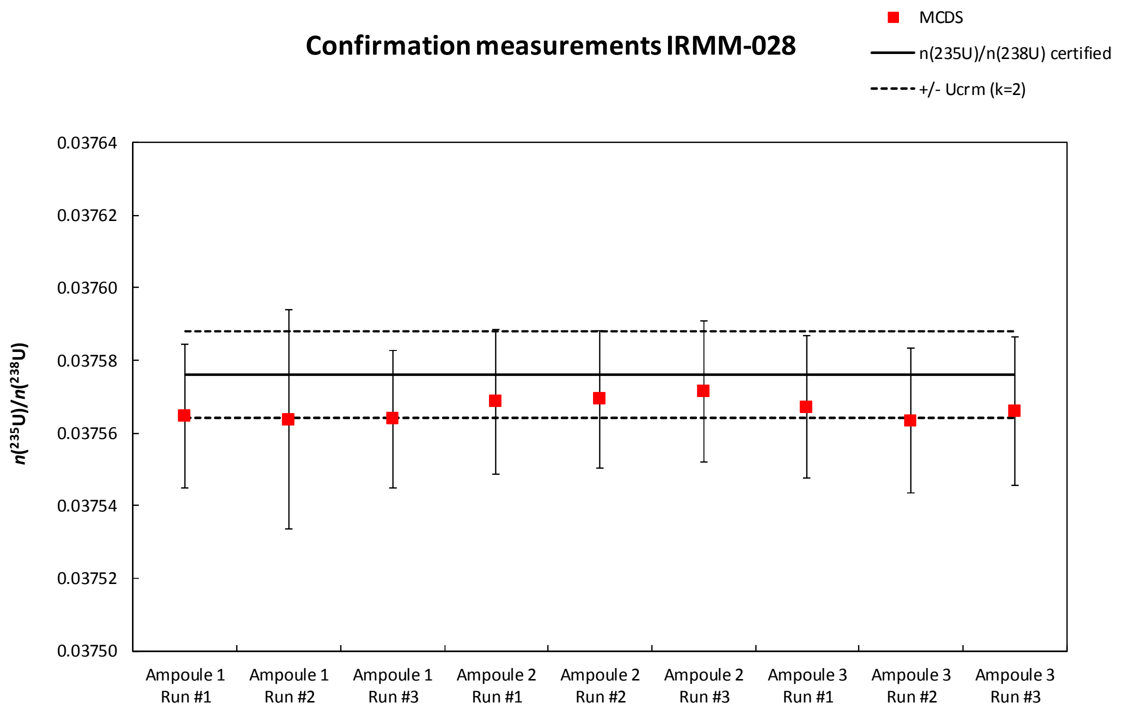




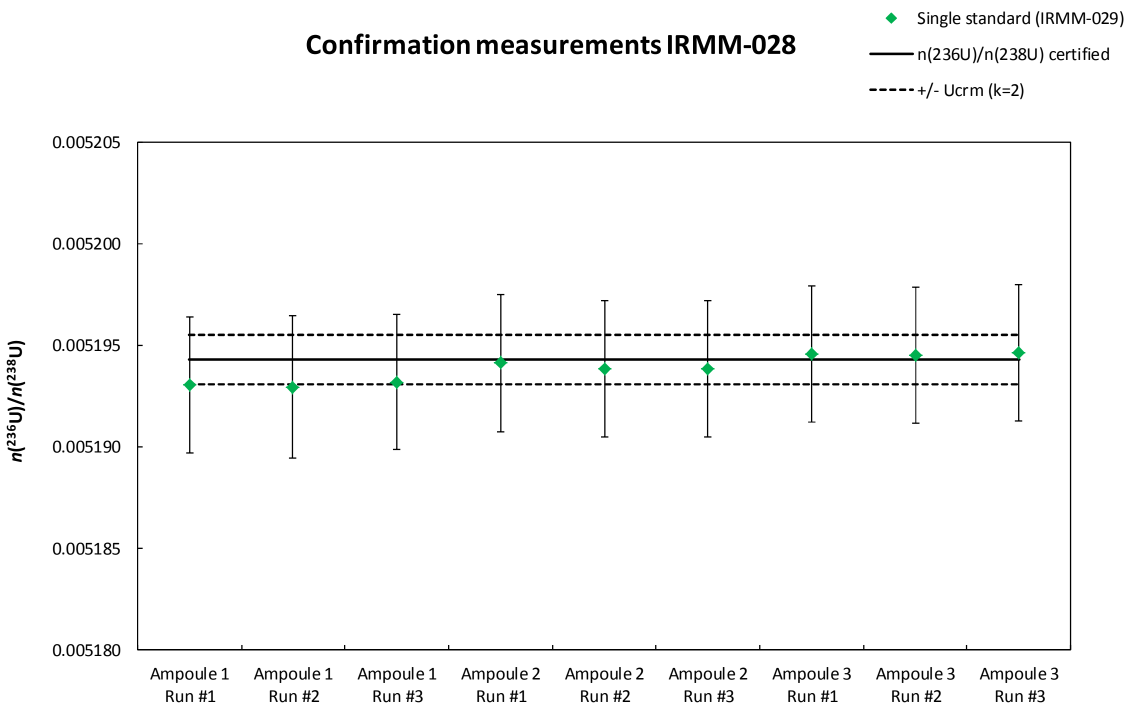


Annex 12.10: Confirmation measurements for IRMM-028



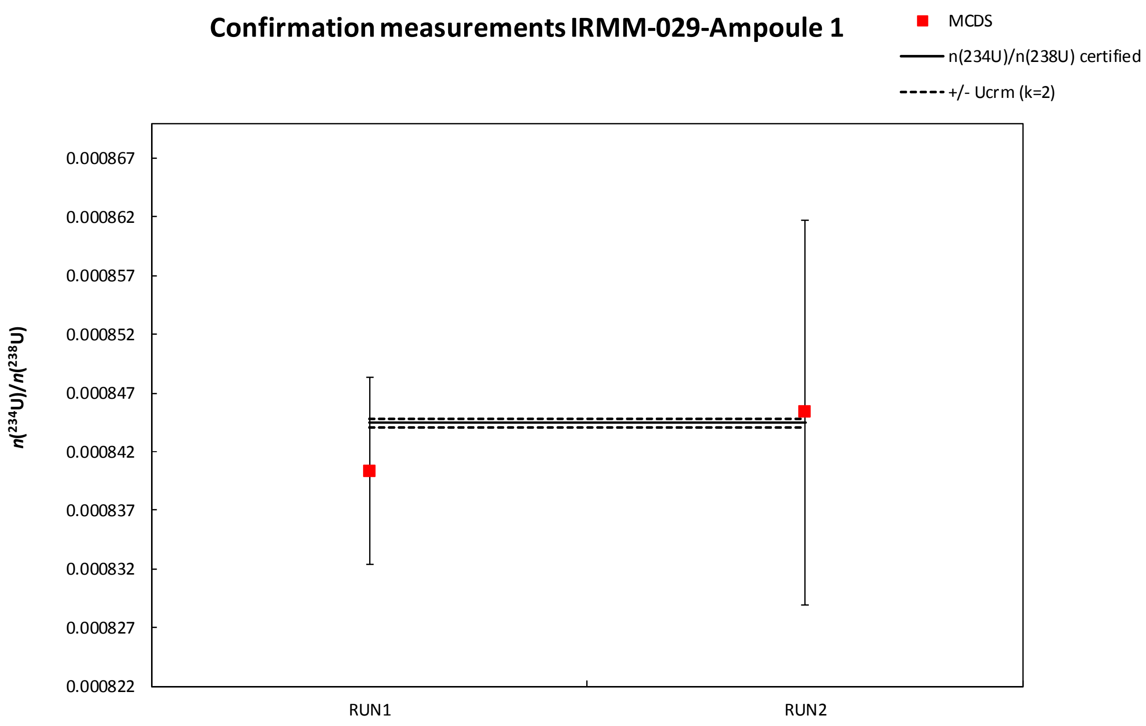


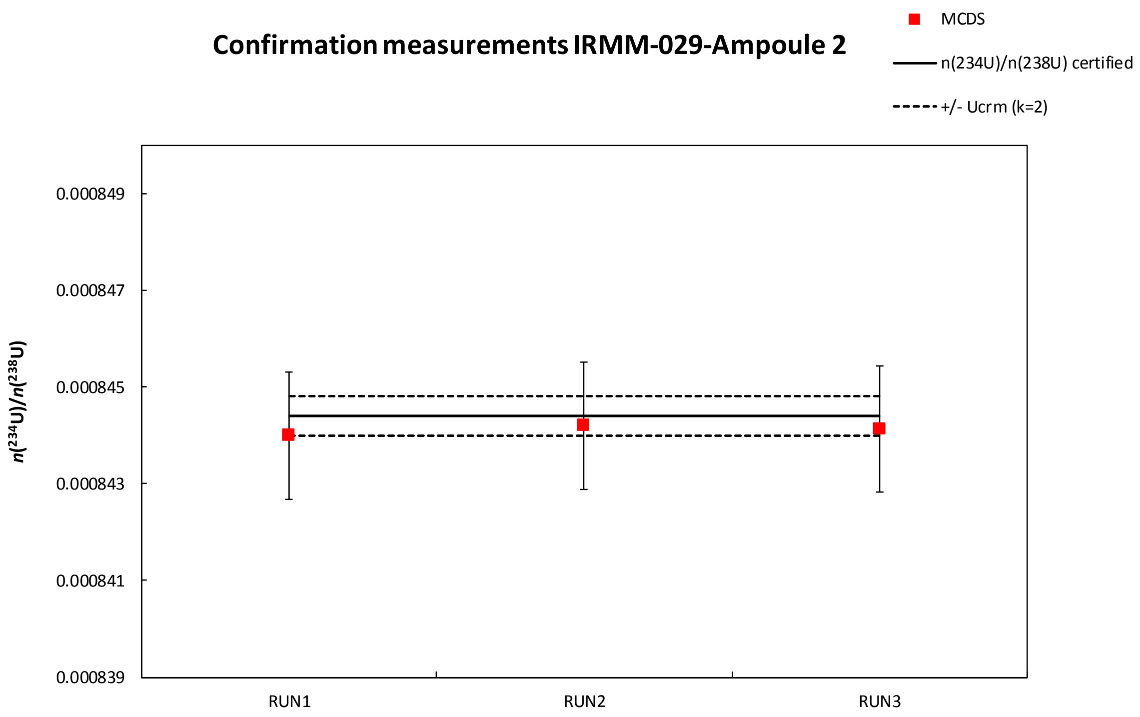
Confirmation measurements IRMM-028
MCDS
n(235U)/n(238U) certified
+/- Ucrm (k=2)
0.03764
0.03762
0.03760
0.03758
0.03756
0.03754
0.03752
0.03750
n(235U)/n(238U)
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3

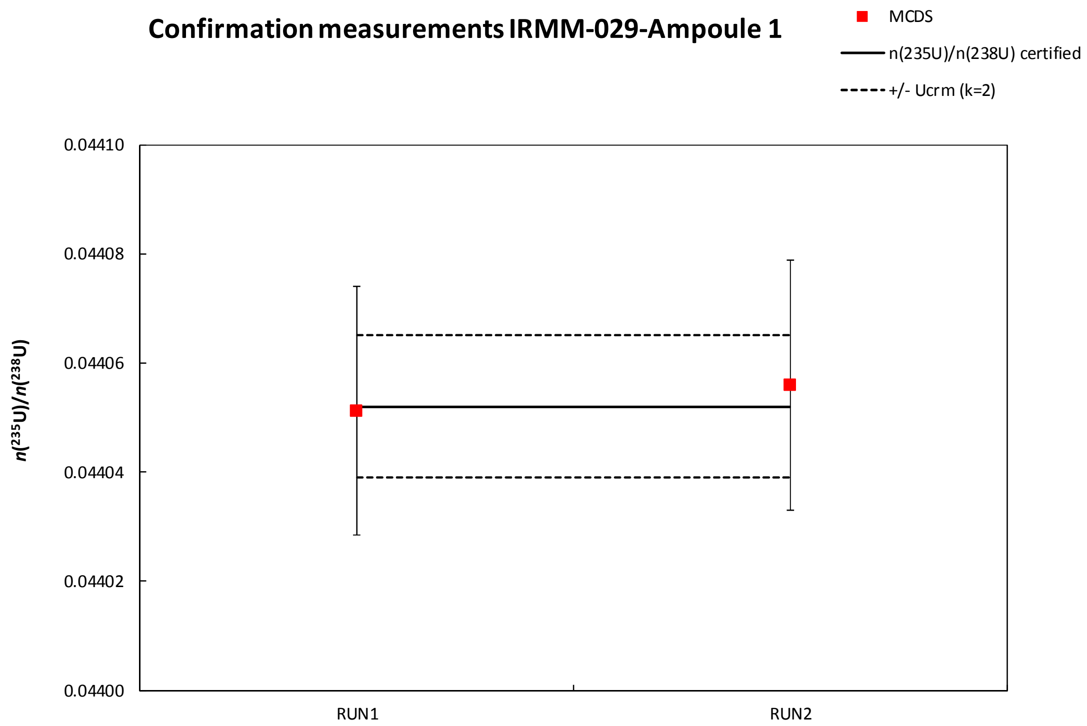


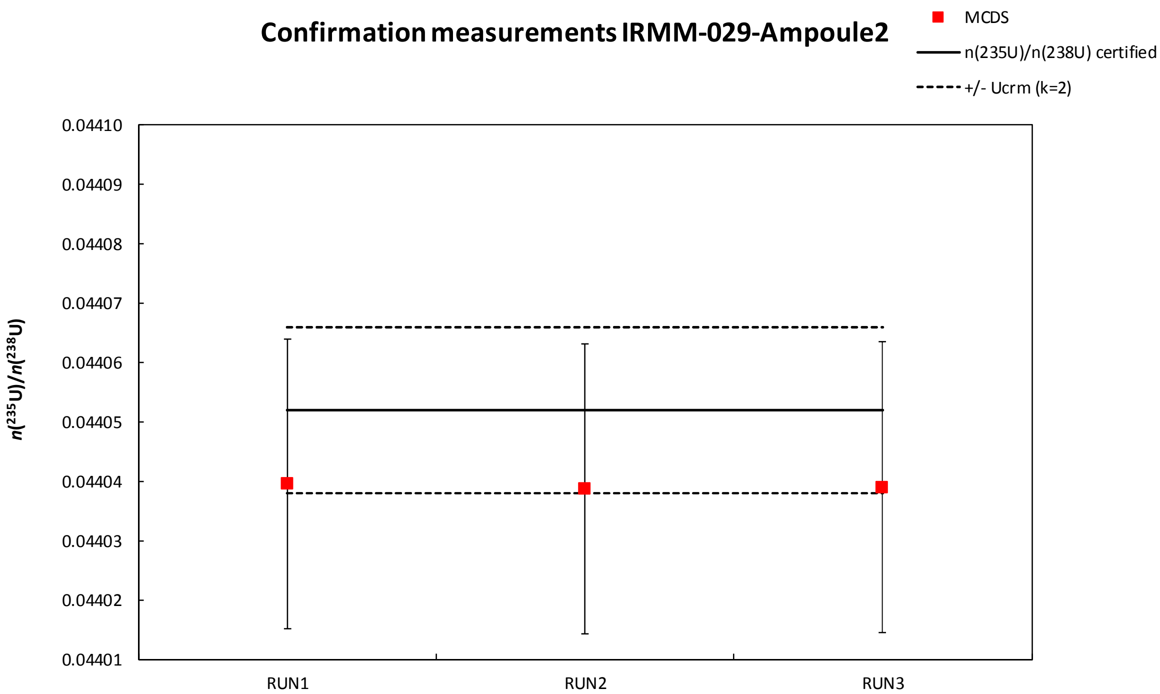
Confirmation measurements IRMM-028
Single standard (IRMM-029)
n(236U)/n(238U) certified
+/- Ucrm (k=2)
0.005205
0.005200
0.005195
0.005190
0.005185
0.005180
n(236U)/n(238U)
Ampoule 1 Run #1
Ampoule 1 Run #2
Ampoule 1 Run #3
Ampoule 2 Run #1
Ampoule 2 Run #2
Ampoule 2 Run #3
Ampoule 3 Run #1
Ampoule 3 Run #2
Ampoule 3 Run #3

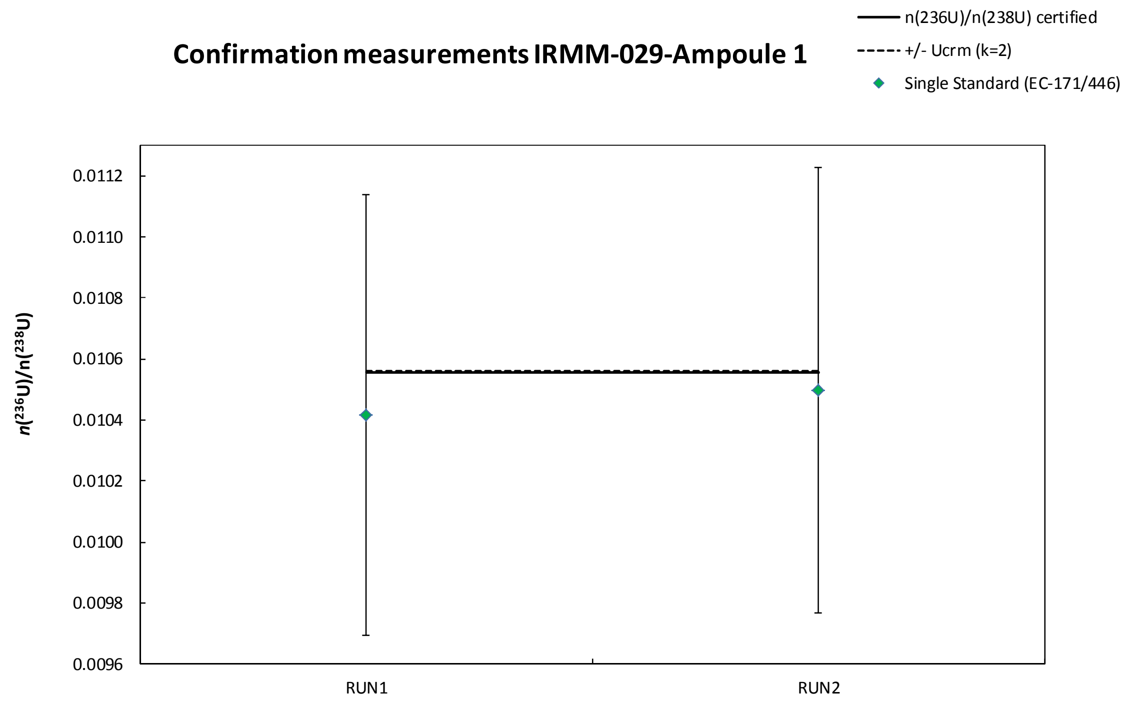
Annex 12.11: Confirmation measurements for IRMM-029

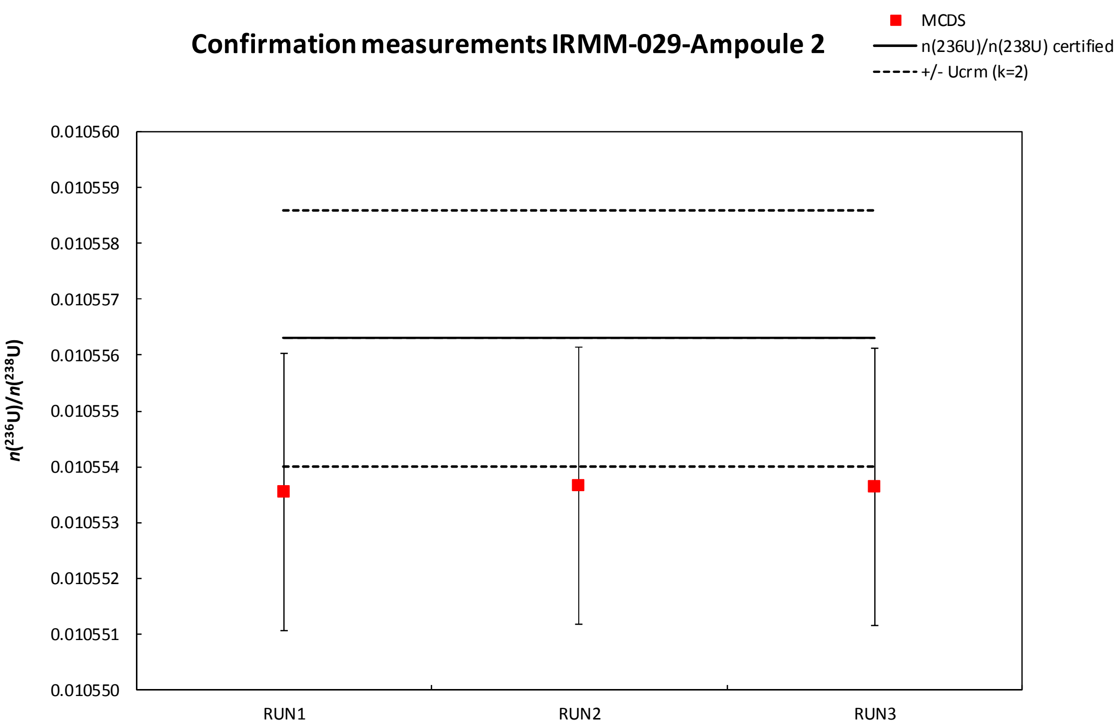





Confirmation measurements IRMM-029-Ampoule 1
MCDS
n(235U)/n(238U) certified
+/- Ucrm (k=2)
$n(^{235}U)/n(^{238}U)$
0.04410
0.04408
0.04406
0.04404
0.04402
0.04400
RUN1
RUN2


Confirmation measurements IRMM-029-Ampoule2
MCDS
n(235U)/n(238U) certified
+/- Ucrm (k=2)
$n(^{235}U)/n(^{238}U)$
0.04410
0.04409
0.04408
0.04407
0.04406
0.04405
0.04404
0.04403
0.04402
0.04401
RUN1
RUN2
RUN3


Confirmation measurements IRMM-029-Ampoule 1
n(236U)/n(238U) certified
+/- Ucrm (k=2)
Single Standard (EC-171/446)
$n(^{236}U)/n(^{238}U)$
0.0112
0.0110
0.0108
0.0106
0.0104
0.0102
0.0100
0.0098
0.0096
RUN1
RUN2


Confirmation measurements IRMM-029-Ampoule 2
MCDS
n(236U)/n(238U) certified
+/- Ucrm (k=2)
$n(^{236}U)/n(^{238}U)$
0.010560
0.010559
0.010558
0.010557
0.010556
0.010555
0.010554
0.010553
0.010552
0.010551
0.010550
RUN1
RUN2
RUN3

European Commission
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Title: **Certification of the uranium hexafluoride (UF6) isotopic composition: The IRMM-019 to IRMM-029 series**

Author(s): S. Mialle, S. Richter, J. Truyens, C. Hennessy, U. Jacobsson, Y. Aregbe

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Abstract

This report describes the re-determination and certification of the IRMM-019 to IRMM-029 series of uranium hexafluoride (UF6) reference materials certified for the uranium isotopic composition. The values were assigned following ISO Guide 34:2009.
The IRMM-019 to IRMM-029 series was originally produced and certified in the 1980's-1990's. Since, the materials are stored in monel ampoules. Upon customer request, UF6 gas is distilled from a mother ampoule into a daughter ampoule, the isotopic composition is verified by Gas Source Mass Spectrometry (GSMS) and the daughter ampoule is sent to the customer. For the purpose of this project, the UF6 materials were converted into uranium nitrate solutions to perform the homogeneity and characterisation studies. Between-unit homogeneity was quantified and stability during dispatch and storage were assessed in accordance with ISO Guide 35:2006.
The materials were characterised by Thermal Ionisation Mass Spectrometry (TIMS) using newly established measurement procedures such as the Modified Total Evaporation (MTE) and Double Spike (DS) methods, and with a new set of certified uranium isotope reference materials, which were prepared by gravimetrical mixing of highly enriched 233U, 235U, 236U and 238U oxides or solutions. The results of the characterisation measurements were also confirmed by GSMS measurements using the original UF6 gases.
Uncertainties of the certified values were estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [ ] and include uncertainties related to the characterisation measurements and the homogeneity study.
The materials are intended for the calibration of methods, quality control purposes, and the assessment of method performance for isotope mass spectrometry. As with any certified reference material, they can also be used for validation studies. The CRMs are available in monel ampoules. Based on physical reasons, there is no minimum sample intake to be taken into account..

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